

Organic Chemistry Part 2

CHAPTER 4

Alcohols, Phenols and Ethers

4.1–4.82

4.1	Introduction	4.1
4.2	Classification of Alcohols and Phenols	4.1
4.3	IUPAC and Common Names of Some Alcohols and Phenols	4.2
4.3.1	Classification of Ethers	4.3
4.3.2	Naming of Polyethers and Cyclic Ethers	4.3
4.3.3	Crown Ethers	4.5
4.3.4	Uses of Ethers	4.5
4.4	Comparison Between the Structures of Alcohols, Phenols, and Ethers	4.6
4.5	Commercial and Industrial Methods for the Synthesis of Methanol and Ethanol	4.7
4.6	Different Types of Industrial Alcohols	4.7
4.6.1	Alcoholic Proof	4.8
4.7	Preparation of Alcohols	4.8
4.7.1	Some Examples	4.8
4.7.2	From Alkyl Halide with Ag_2O in H_2O	4.9
4.7.3	From Grignard Reagents (G.R.)	4.9
4.7.4	From Carbonyl Compounds	4.9
4.7.5	Oxymercuration-demercuration (OMDM) Reaction for the Preparation of Alcohols and Hydroboration Oxidation for the Preparation of Alcohol	4.10
4.7.6	Treating Haloalkene with Moist Ag_2O or $(\text{AgCl} + \text{H}_2\text{O})$ to give Alcohol	4.10
4.8	Physical Properties	4.10
4.9	Dihydric Alcohols	4.11
4.9.1	Ethylene Glycol or Ethane-1,2-Diol	4.11
4.9.2	Trihydric Alcohols: Glycerol or Glycerine 1,2,3-Propanetriol	4.11
4.10	Preparation of Phenols	4.12
4.11	Chemical Reactions of Alcohols	4.17
4.11.1	Reactions Involving Cleavage of (O—H) Bond	4.18
4.11.2	Acidity of Alcohols	4.18

4.11.3 Reactions Involving Cleavage of (C—O) Bond in Alcohols	4.19
4.12 Dehydration	4.19
4.13 Comparison of Acidic Character of Thiols and Alcohols	4.20
4.14 Acidity of Phenols	4.20
4.15 Some Reactions of Phenols	4.23
4.16 Reaction of Phenol with HNO_2 or ($\text{NaNO}_2 + \text{HCl}$ at $0-5^\circ\text{C}$)	4.25
4.17 Dakin Reaction	4.25
4.17.1 Mechanism	4.25
4.18 Elbs Persulphate Oxidation	4.26
4.18.1 Mechanism	4.26
4.19 Houben–Hoesch Synthesis	4.26
4.19.1 Mechanism	4.26
4.20 Reimer–Tiemann Reaction	4.26
4.20.1 Mechanism	4.26
4.20.2 Mechanism of the Reimer Tiemann Reaction on Indole	4.26
4.20.3 Extension of Reimer-Tiemann	4.27
4.21 Kolbe–Schmitt Reaction	4.27
4.21.1 Mechanism	4.27
4.22 Vilsmeier Reaction	4.29
4.23 Reaction of Phenol with an Aldehyde	4.29
4.24 Bimolecular Reduction of Carbonyl Compound to Vicinal diol	4.30
4.24.1 Mechanism	4.30
4.25 Pinacol–Pinacolone Rearrangement Reaction	4.30
4.25.1 Mechanism	4.30
<i>Concept Application Exercise 4.1</i>	4.33
4.26 Preparation of Ethers	4.34
4.26.1 Dehydration of Alcohols Under Different Conditions	4.34
4.26.2 Limitations	4.35
4.27 Williamson Synthesis	4.35
4.28 Some Other Methods for the Preparation of Ethers	4.36
4.28.1 Mechanism	4.37
4.28.2 Commercial Synthesis of Diphenyl Ether	4.37
4.29 Physical Properties of Ethers	4.39
4.30 Chemical Reactions of Ethers	4.39
4.30.1 Mechanism (When Both Alkyl Groups Are 1° , the Halide Formed Is with Smaller Alkyl Group)	4.39
4.30.2 Mechanism When One of the Alkyl Groups is 3°	4.40
4.30.3 Mechanism in Case of Anisole	4.40
4.31 Reaction of Ether by Aqueous HI and Anhydrous HI	4.40
4.32 Formation of Coordination Complexes	4.41
4.32.1 Reaction of Ether with H_2SO_4	4.42
4.32.2 Reaction of Ether with PCl_5	4.42

4.32.3	Ether's Reaction with Acid Chlorides and Anhydrides	4.42
4.32.4	Reactions Involving Alkyl Group	4.42
4.32.5	Halogenation	4.42
4.33	Zeisel Method for the Determination of Methoxy Groups	4.43
4.34	Claisen Rearrangement Reaction	4.43
4.34.1	Mechanism	4.43
4.34.2	para-Migration	4.43
4.35	Alkoxy Mercuration-Demercuration (A Type of Solvomercuration–Demercuration)	4.45
4.36	SE (Substitution by Electrophile) Reactions	4.45
4.36.1	Nitration	4.45
4.36.2	Halogenation	4.46
4.36.3	Friedel–Crafts Reaction	4.46
4.37	Fries Rearrangement Reaction	4.46
4.38	Epoxides (Oxiranes)	4.49
	<i>Concept Application Exercise 4.2</i>	4.50
	<i>Exercises</i>	4.51
	<i>Single Correct Answer Type</i>	4.51
	<i>Multiple Correct Answers Type</i>	4.66
	<i>Linked Comprehension Type</i>	4.72
	<i>Matrix Match Type</i>	4.75
	<i>Numerical Value Type</i>	4.78
	<i>Archives</i>	4.79
	<i>Answers Key</i>	4.81

4

Alcohols, Phenols and Ethers

4.1 INTRODUCTION

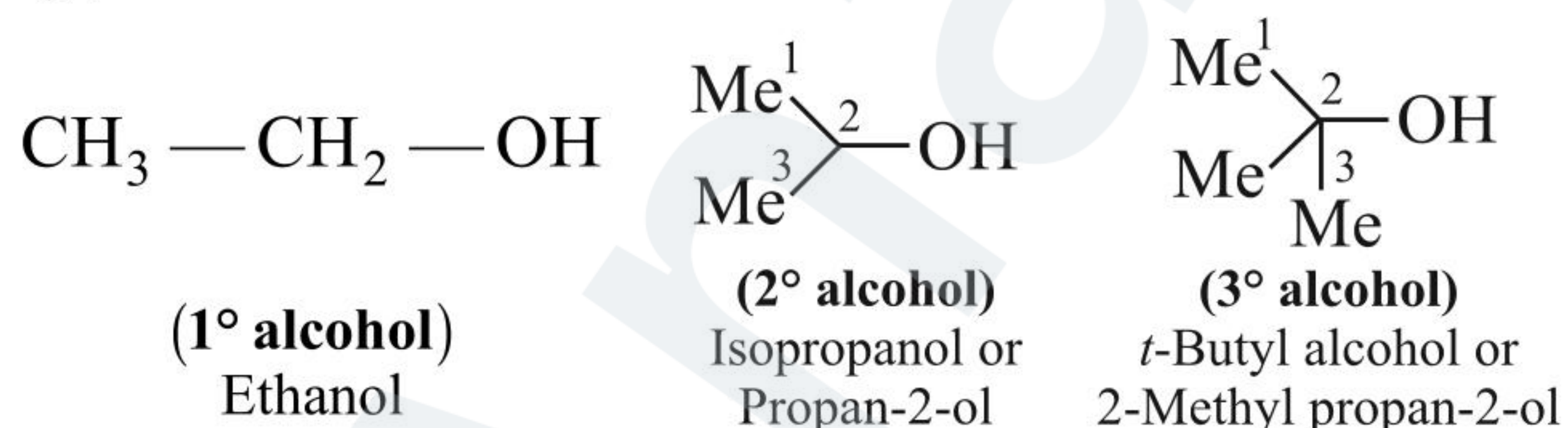
Alcohols and phenols are formed when an H atom in aliphatic and aromatic hydrocarbon is replaced by (—OH) group. An alcohol contains one or more hydroxyl (—OH) group(s) directly attached to C atom(s) of an aliphatic system (e.g., CH₃OH), while a phenol contains (—OH) group(s) directly attached to C atom(s) of an aromatic system (e.g., PhOH).

Ethers are formed when an H atom in a hydrocarbon is replaced by an alkoxy (—OR) or aryloxy (—OAr) group, for example, MeOMe (methoxy methane or dimethyl ether) and PhOMe (anisole) or (methoxybenzene).

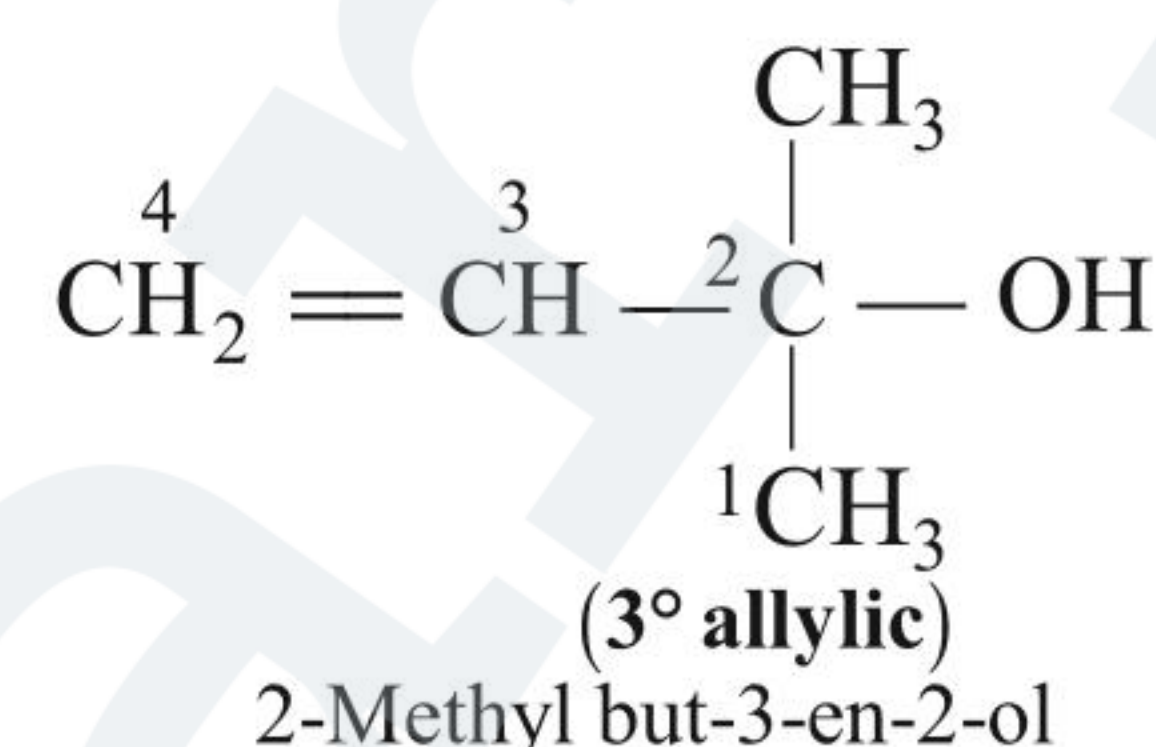
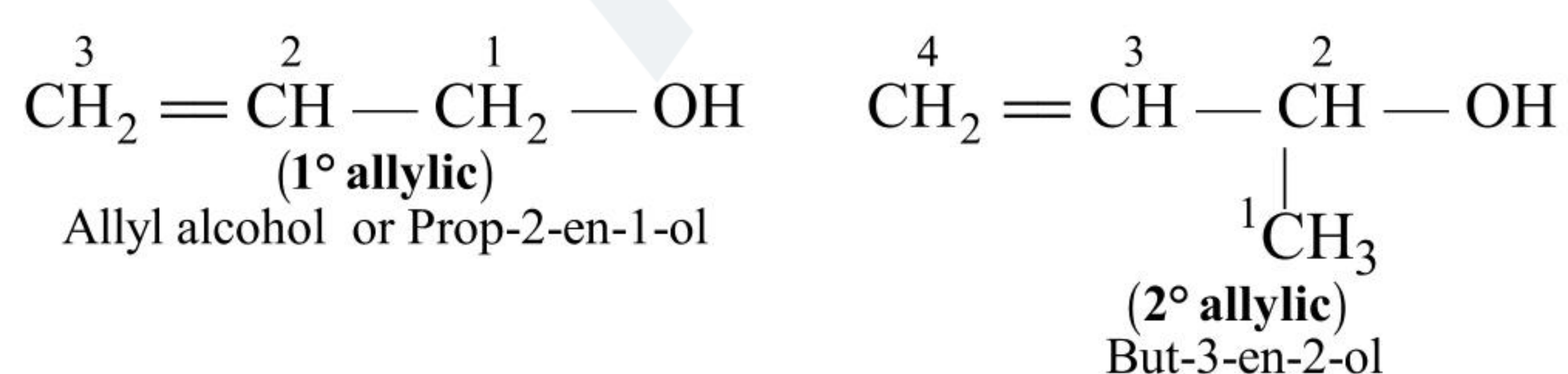
Alcohols, phenols, and ethers are the basic compounds for the formation of antiseptics, fragrances, and detergents. These compounds are widely used in industry and day-to-day life. For example, spirit (C₂H₅OH) is used for polishing wooden furniture. Sugar, cotton, and paper are all made up of compounds containing (—OH) groups.

4.2 CLASSIFICATION OF ALCOHOLS AND PHENOLS

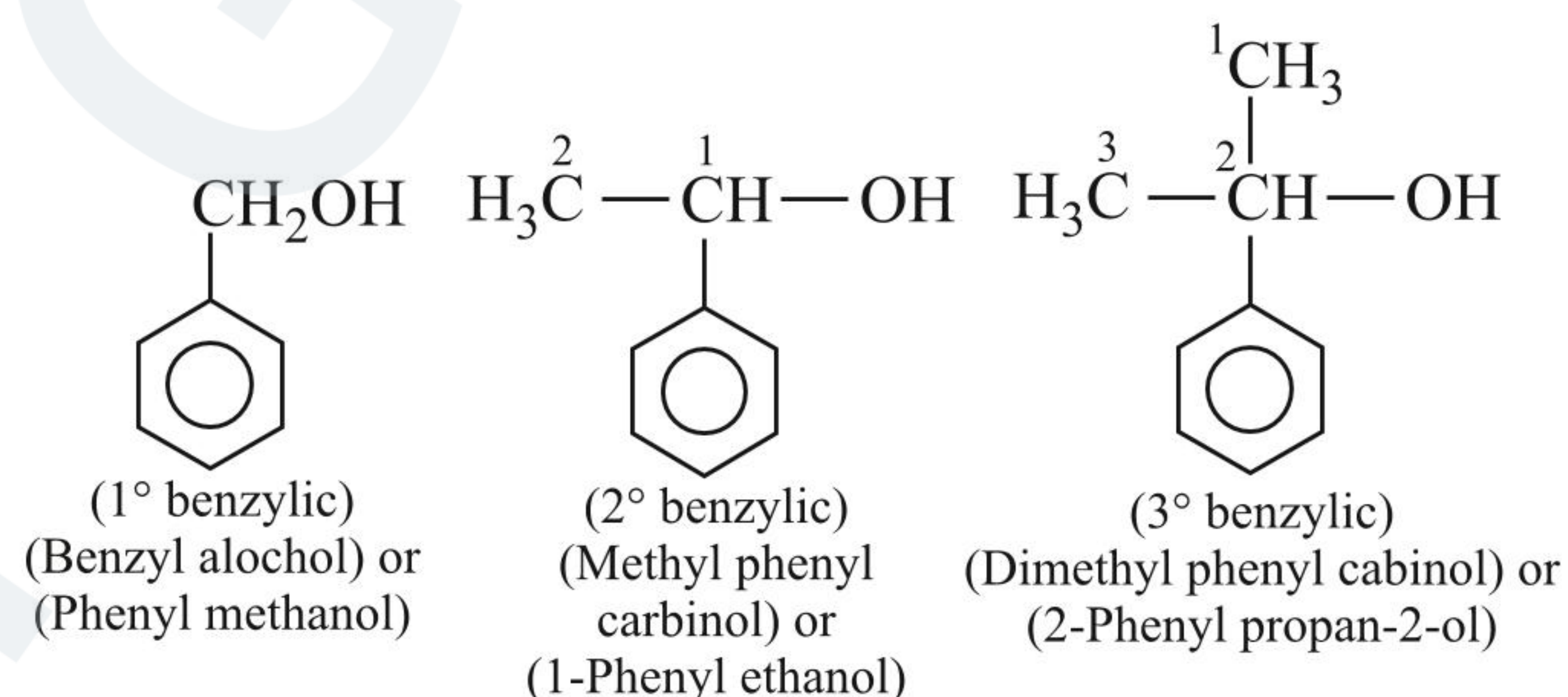
- a. Compounds containing (*sp*³ C—OH):** These are the compound in which (—OH) group is attached to an *sp*³-hybridised C atom of an alkyl group. They are further classified as 1°, 2°, and 3° alcohols in which the (—OH) group is attached to 1°, 2°, and 3° C atom, respectively, e.g.,



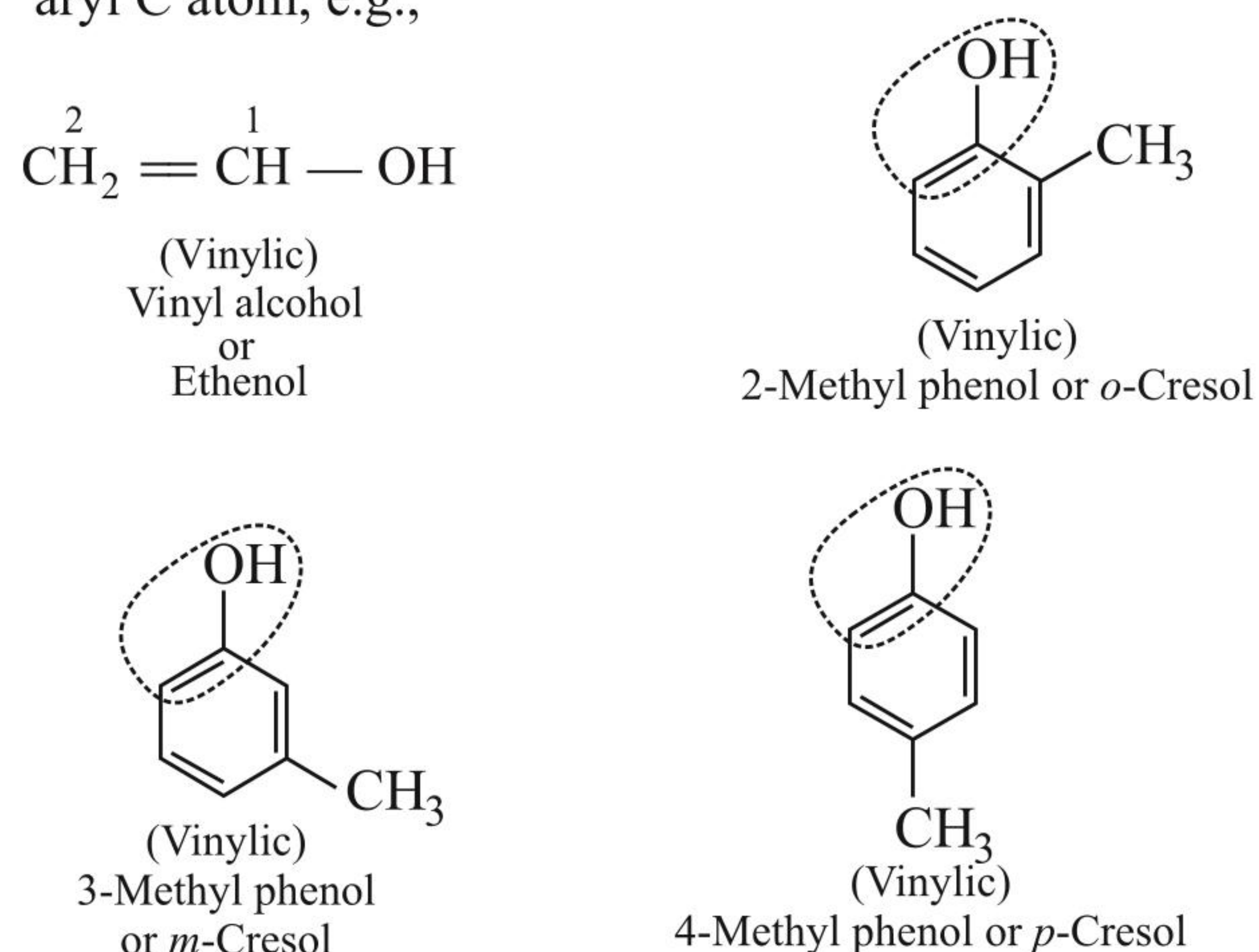
- b. Allylic alcohols:** The (—OH) group is attached to an *sp*³-hybridised C atom next to (C=C) bond, i.e., an allylic C atom, e.g.,



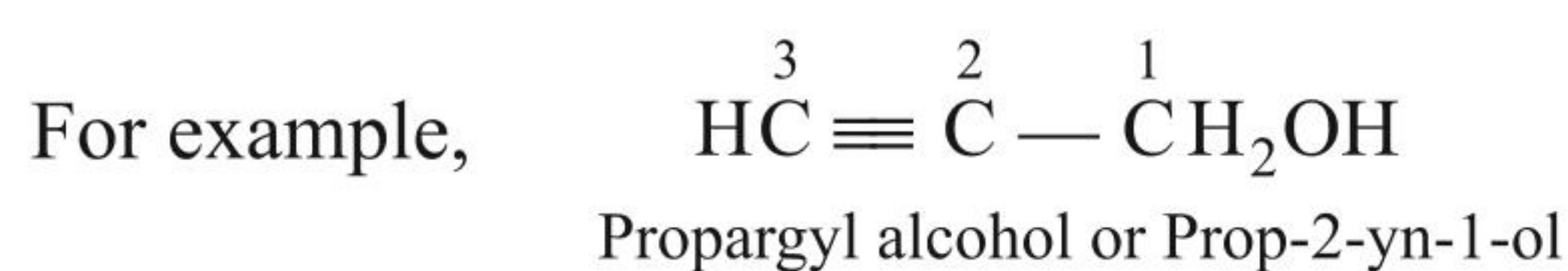
- c. Benzylic alcohols:** The (—OH) group is attached to an *sp*³-hybridised C atom next to an aromatic ring, e.g.,



- d. Compounds containing *sp*² (C—OH) bond:** The (—OH) group is attached to (C=C), i.e., to vinylic C atom or to an aryl C atom, e.g.,

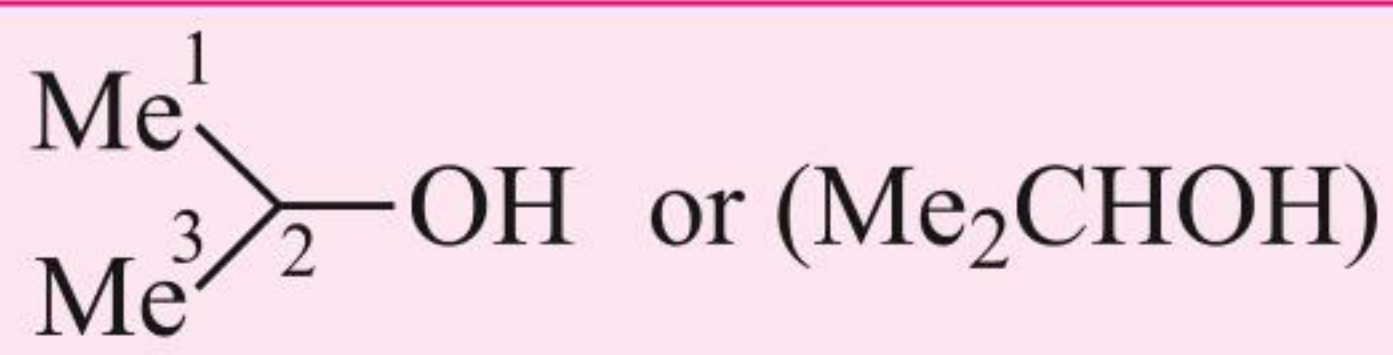

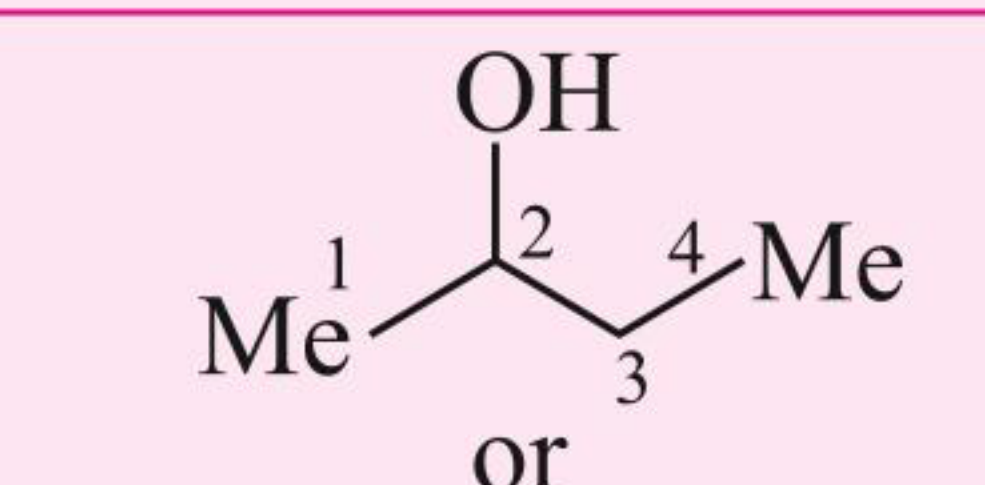
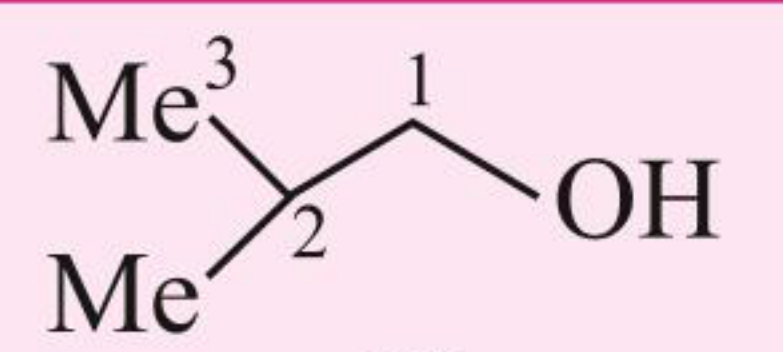
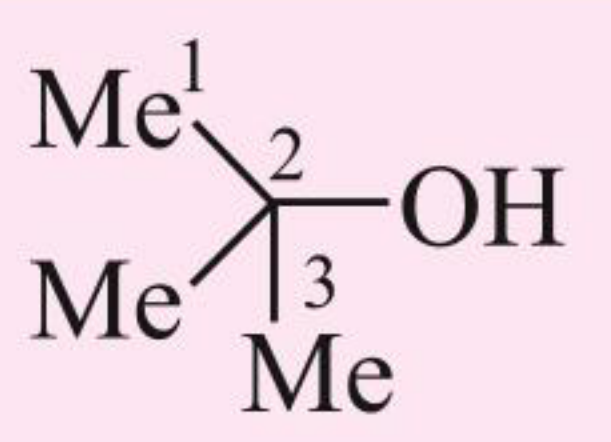

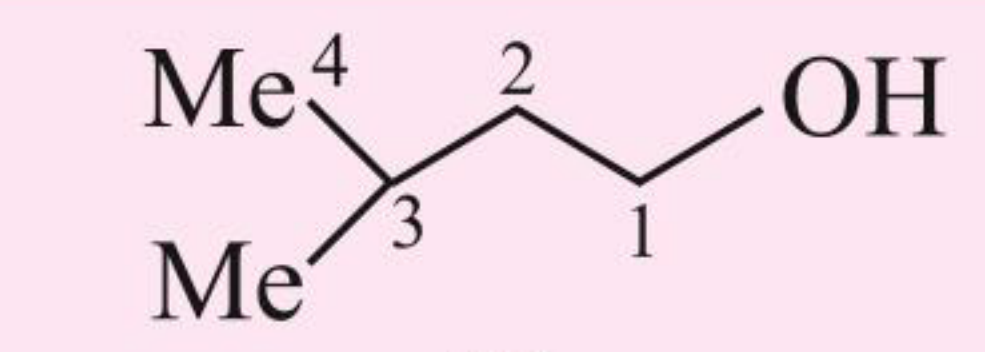
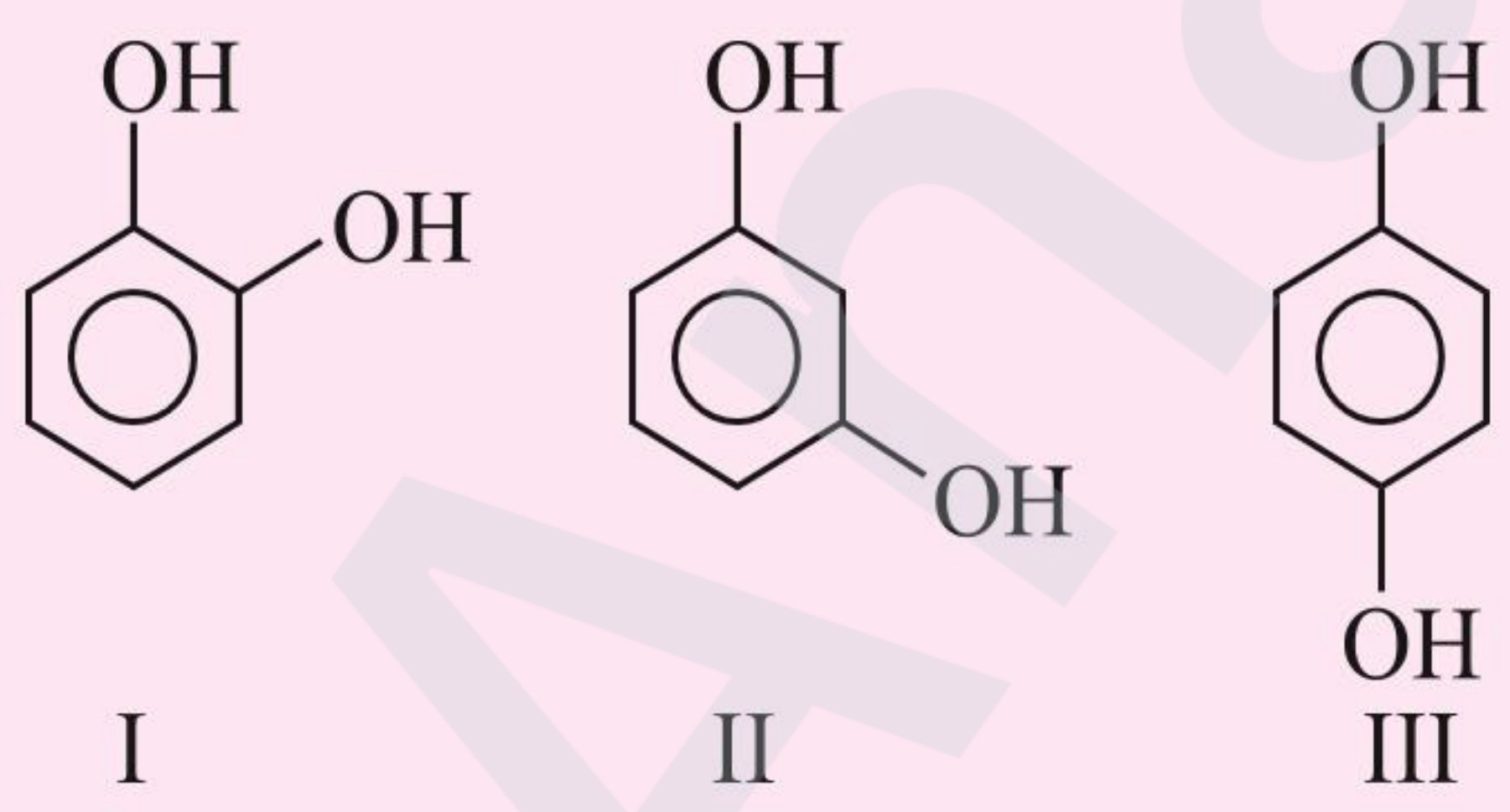
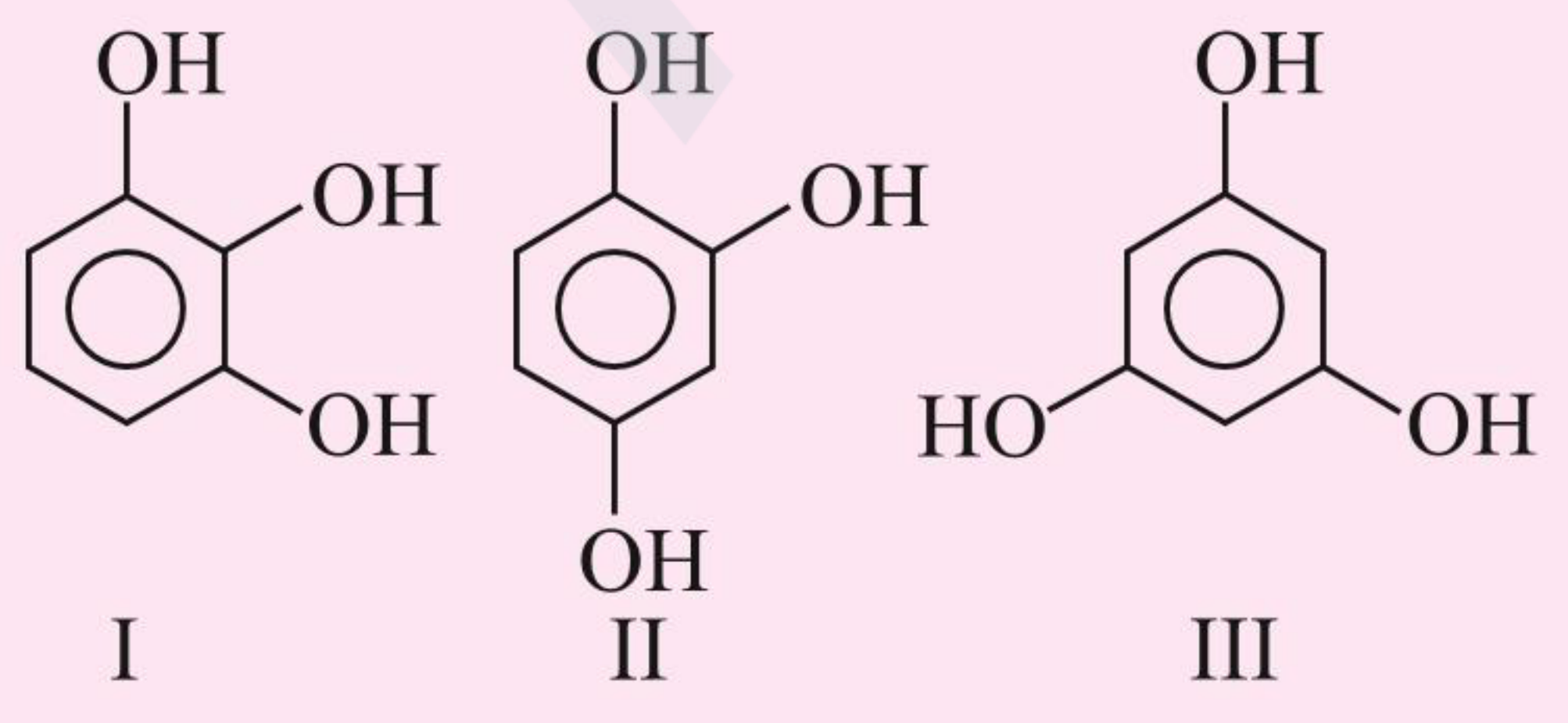


- e. Compounds containing *sp* (C—CH₂—OH):** The (—OH) group is attached to the next C atom attached to (C≡C) bond, i.e., propargylic C atom.



4.3 IUPAC AND COMMON NAMES OF SOME ALCOHOLS AND PHENOLS

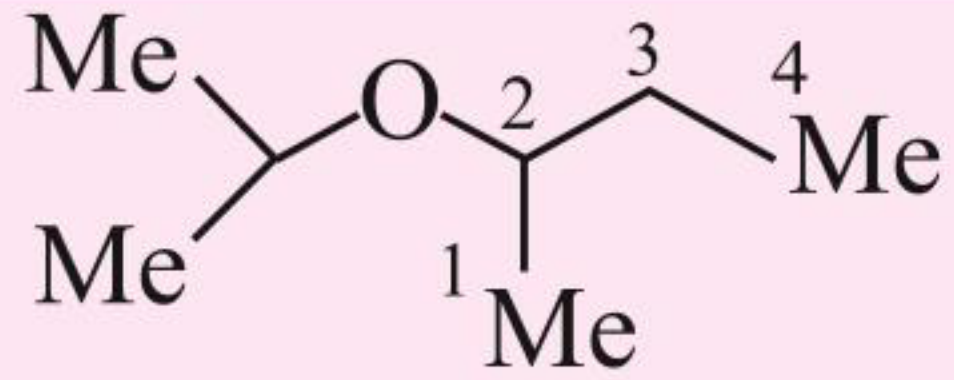
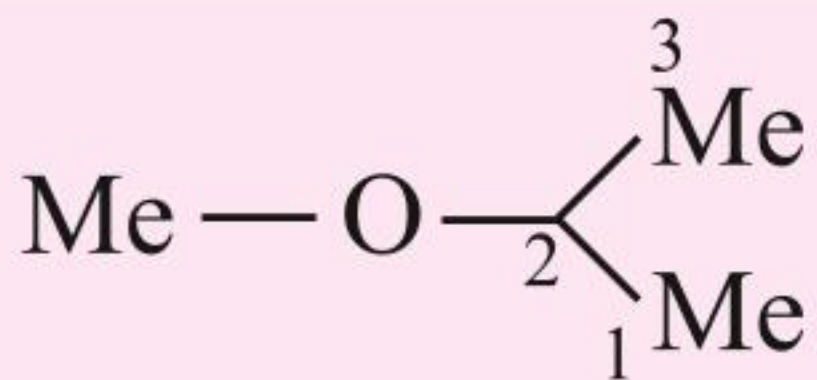
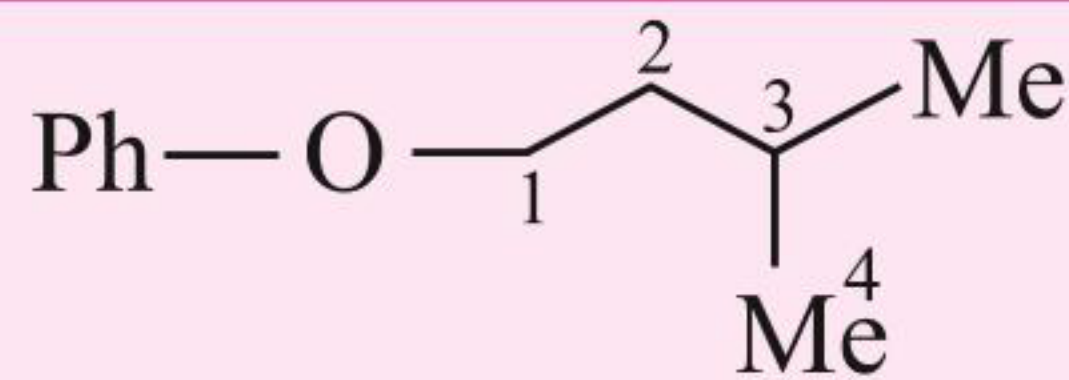
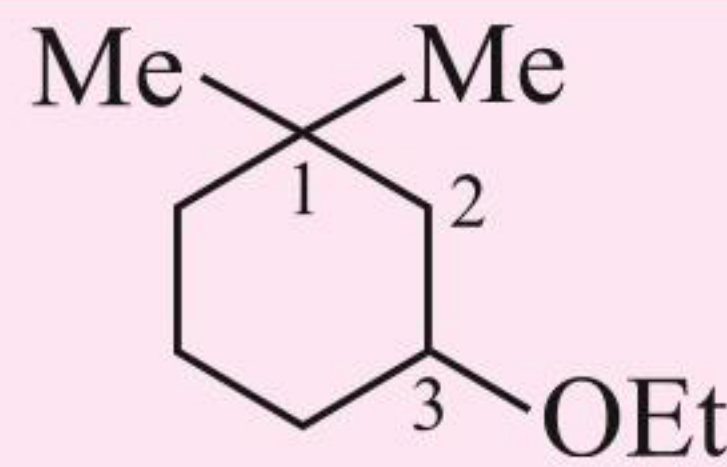

Table 4.1 IUPAC and common names of some alcohols and phenols

S.No.	Compound	IUPAC name or trivial name	Common or systematic
1.	$\text{CH}_3 - \text{OH}$	Methanol or Zerone	Methyl alcohol or Carbinol
2.	 Me_2CHOH or (Me_2CHOH)	Propan-2-ol	Isopropyl alcohol
3.	 or $(\text{MeCH}_2\text{CH}_2\text{CH}_2\text{OH})$	Butan-1-ol	<i>n</i> -Butyl alcohol
4.	 or $\text{MeCH}(\text{OH})\text{CH}_2\text{Me}$	Butan-2-ol	<i>sec</i> -Butyl alcohol
5.	 or $\text{Me}_2\text{CHCH}_2\text{OH}$	2-Methyl propan-1-ol	Isobutyl alcohol
6.	 or $\text{Me}_3\text{C} - \text{OH}$	2-Methyl propan-2-ol	<i>tert</i> -Butyl alcohol
7.	 or $\text{Me}(\text{CH}_2)_4\text{OH}$	Pentan-1-ol	<i>n</i> -Amyl alcohol or <i>n</i> -Pentanol or <i>n</i> -Pentyl alcohol
8.	 or $\text{Me}_2\text{CHCH}_2\text{CH}_2\text{OH}$	3-Methyl butan-1-ol	Isoamyl alcohol or Isopentanol
9.	 I II III	I = Benzene-1,2-diol II = Benzene-1,3-diol III = Benzene-1,4-diol	I = Catechol II = Resorcinol III = Quinol or Hydroquinone
10.	 I II III	I = Benzene-1,2,3-triol II = Benzene-1,2,4-triol III = Benzene-1,3,5-triol	I = Pyrogallol II = Hydroxy quinol III = Phloroglucinol

4.3.1 Classification of Ethers

If the two alkyl or aryl groups attached to the O atom are same, they are called **simple** or **symmetrical** ethers. If the alkyl or aryl groups attached to the O atom are different, they are called **mixed** or **unsymmetrical** ethers.

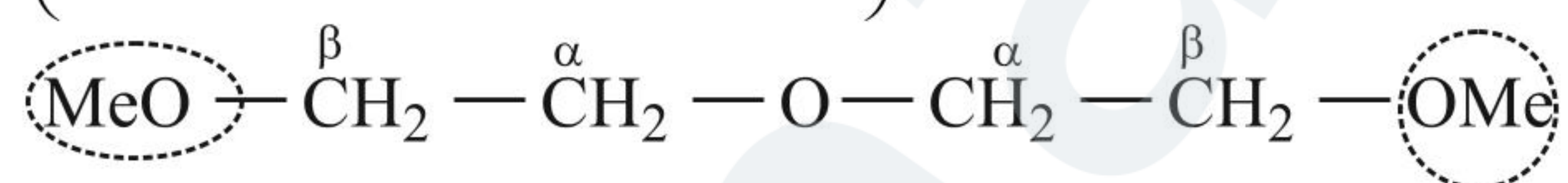
Table 4.2 IUPAC and common names of some ethers

S.No.	Compound	IUPAC name or trivial name	Common or systematic
1.	$\text{CH}_3\text{—O—CH}_3$ or $(\text{CH}_3)_2\text{O}$ or Me_2O	Methoxy methane	Dimethyl ether
2.	$\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$ or $(\text{C}_2\text{H}_5)_2\text{O}$ or Et_2O	Ethoxy ethane	Diethyl ether
3.		2-Isopropoxybutane	<i>sec</i> -Butyl isopropyl ether
4.	Ph—O—CH_3	Methoxybenzene (anisole)	Anisole or Methyl phenyl ether
5.	$\text{Ph—O—C}_2\text{H}_5$	Ethoxy benzene	Phenetole or Ethyl phenyl ether
6.		2-Methoxy propane	Methyl isopropyl ether
7.		3-Methyl butoxy benzene	Isopentyl phenyl ether
8.	$\text{Me—O—CH}_2\text{—CH}_2\text{—O—Me}$	1,2-Dimethoxy ethane	—
9.		3-Ethoxy-1,1-dimethyl cyclohexane	—
10.		4-Ethoxy nitro benzene	Ethyl- <i>p</i> -nitrophenyl ether

4.3.2 Naming of Polyethers and Cyclic Ethers

a. Glyme naming: 1,2-Dimethoxy ethane

$\left(\text{MeO—CH}_2\text{—CH}_2\text{—OMe} \right)$ is commonly called glyme.

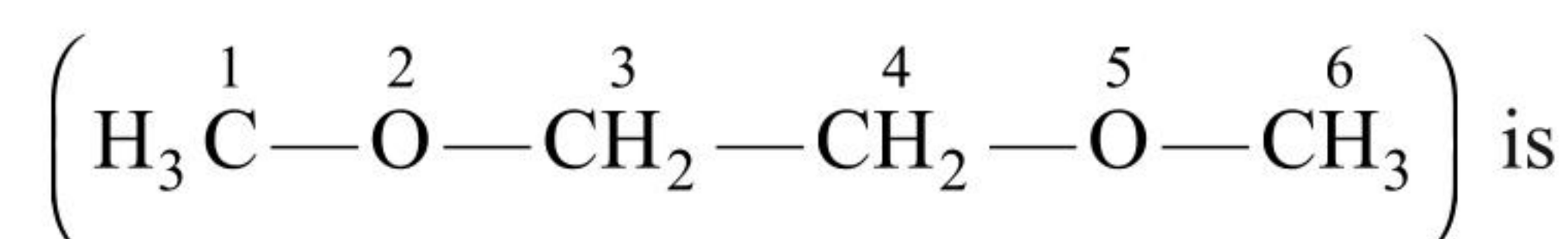


[bis-(β -methoxyl ethyl)] ether is commonly called diglyme.

b. Oxa naming: In Oxa method, O atom of the longest chain or ring is counted as C and it is counted to determine either the

longest C-parent chain or parent ring. Its presence is indicated by the prefix Oxa and a number to designate its position in the chain or ring.

Name of glyme by Oxa method: There are two O atoms and four C atoms; these are taken as six C atoms with the parent chain as hexane; thus the name of glyme



2,5-dioxahexane.

Name of diglyme by Oxa method: $\left(\text{H}_3\overset{1}{\text{C}}\text{—}\overset{2}{\text{O}}\text{—}\overset{3}{\text{CH}_2}\text{—}\overset{4}{\text{CH}_2}\text{—}\overset{5}{\text{O}}\text{—}\overset{6}{\text{CH}_2}\text{—}\overset{7}{\text{CH}_2}\text{—}\overset{8}{\text{O}}\text{—}\overset{9}{\text{CH}_3} \right)$ is 2,5,8-Trioxanonane.

Table 4.3 Common and Oxa names of some cyclic ethers (heterocyclic compounds)

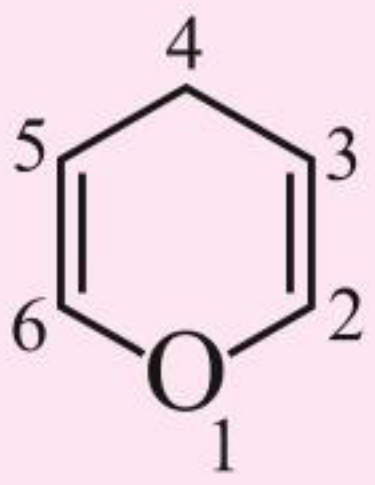
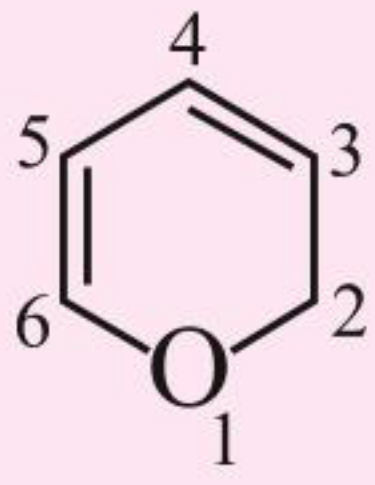
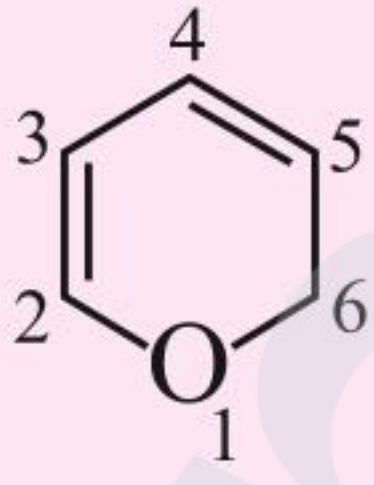
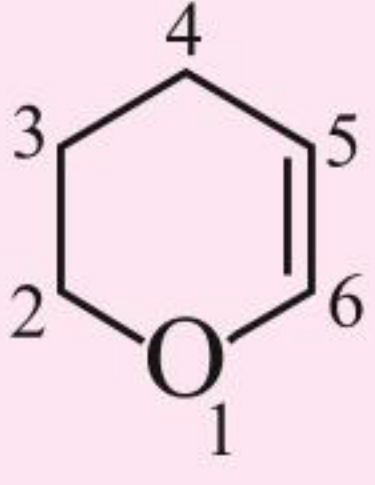
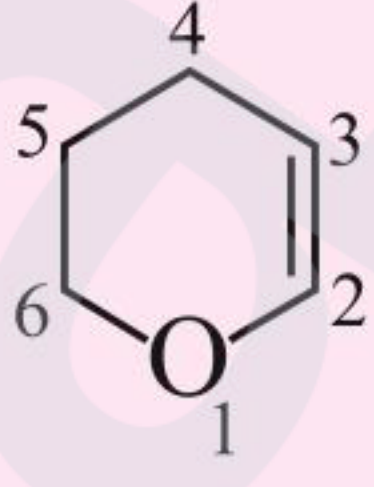
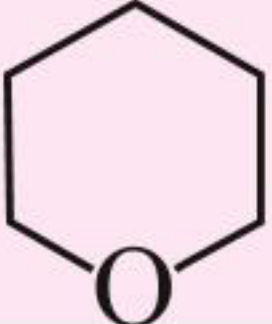
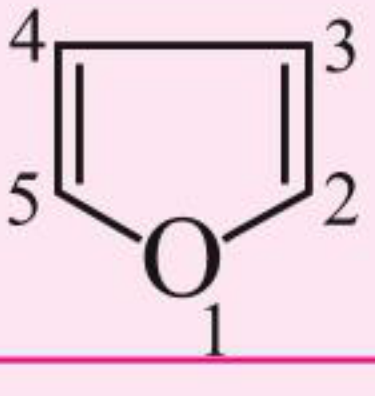

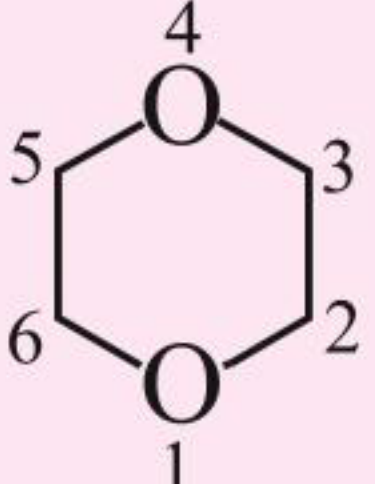
S.No.	Compound	Common name	Oxa name
1.		4H-Pyran: 4H indicates that C-4 is the (CH ₂) group in pyran.	1-Oxa-cyclohexa-2,5-diene
2.		2H-Pyran: 2H indicates that C-2 is the (CH ₂) group in pyran.	 1-Oxa-cyclohexa-2,4-diene
3.		2,3-Dihydro-4H-pyran (DHP): 2,3-Dihydroindicates that two H atoms have been added to 4H-pyran, one to C-2 and one to C-3, or considering the parent structure, the name is 3,4-dihydro-2H-pyran.	 1-Oxa-cyclohex-2-ene
4.		Tetrahydropyran (THP)	Oxacyclohexane
5.		Furan	1-Oxacyclopenta-2,4-diene
6.		Tetrahydrofuran (THF)	Oxacyclopentane
7.		1,4-Dioxane	1,4-Dioxacyclohexane

Table 4.4 IUPAC ring names for cyclic ethers (CH₂)_nO, where *n* = 2 to 6

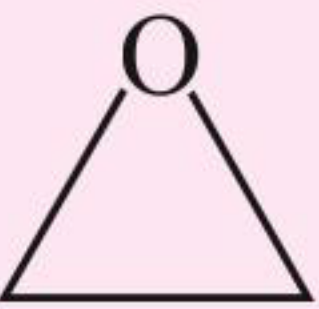
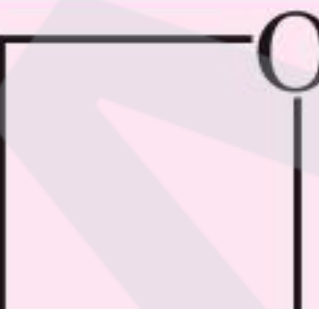

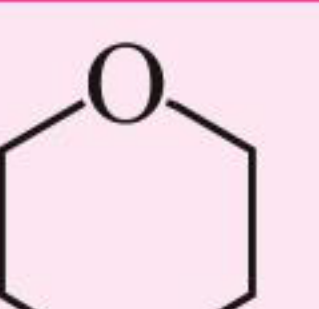
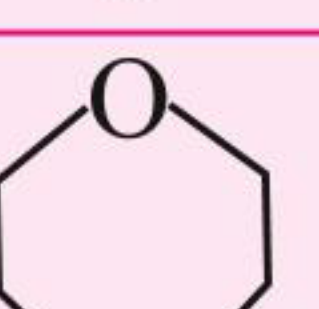

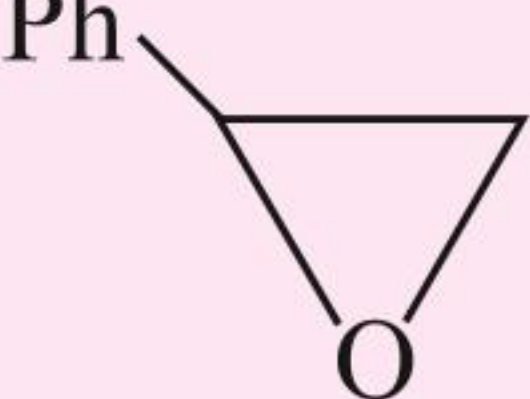
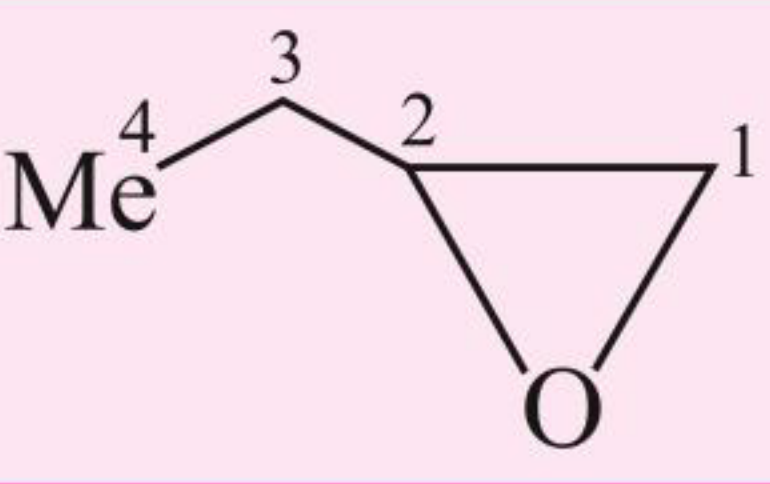
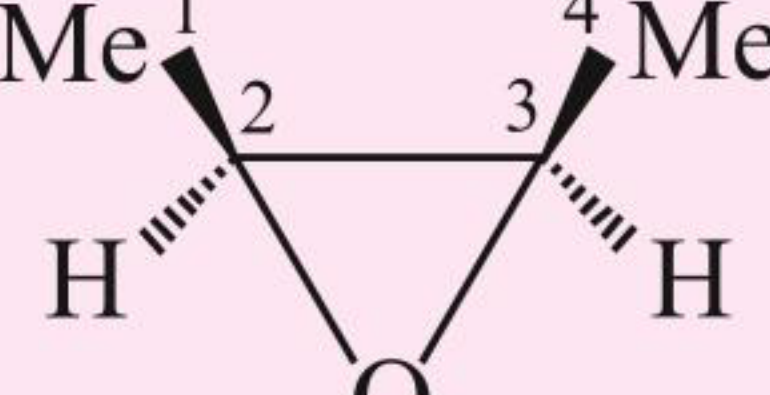
S.No.	Compound	IUPAC name
1.	$n = 2$ 	Oxirane
2.	$n = 3$ 	Oxetane
3.	$n = 4$ 	Oxolane
4.	$n = 5$ 	Oxane
5.	$n = 6$ 	Oxepane

Table 4.5 Oxide or epoxide naming of cyclic ethers (in which oxides of parent alkene are used)

S.No.	Compound	Oxide name
1.		Ethylene oxide or Epoxide
2.		Phenyl ethylene oxide or Styrene oxide (PhCH = CH ₂) (Styrene)
3.		But-1,2-ene oxide or 1,2-Epoxy butane
4.		<i>cis</i> -But-2,3-ene oxide or Z-2,3-Epoxy butane

5.		Methylene cyclopentane oxide
6.		<i>trans</i> -3-Methyl cyclopentene oxide or <i>trans</i> -1,2-Epoxy-3-methyl cyclohexane (oxide ring w.r.t. Me gp.)
7.		<i>cis</i> -3-Ethyl cyclohexene oxide or <i>cis</i> -1,2-Epoxy-3-ethyl cyclohexane (oxide ring w.r.t. Et gp.)

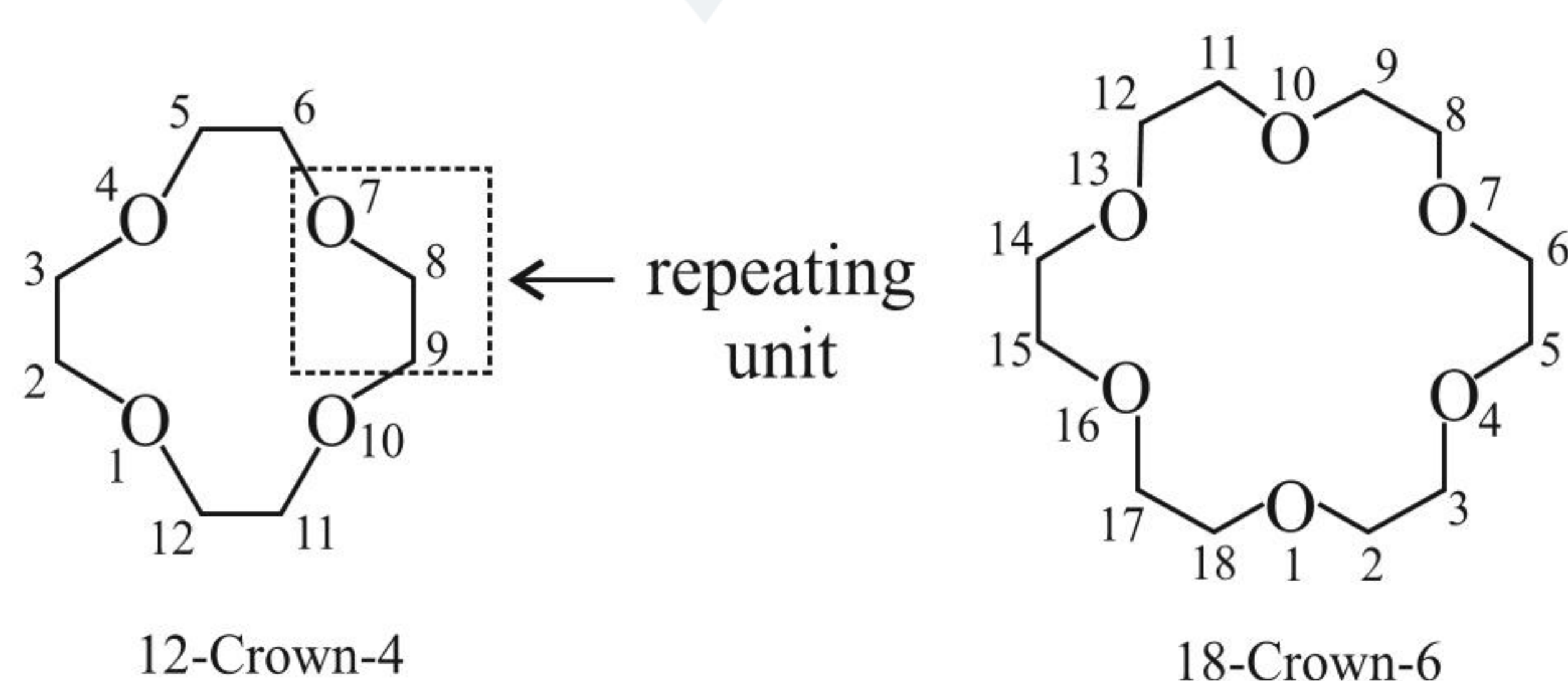
Table 4.6 IUPAC names of some cyclic ethers

S.No.	Compound	IUPAC name
1.		3,3-Dibromo-2-methyl oxetane
2.		2-Oxetene
3.		<i>trans</i> -2,3-Dimethyl oxirane
4.		<i>trans</i> -2-Bromo-5-methyl oxane
5.		<i>cis</i> -2,7-Dichloro oxepane

4.3.3 Crown Ethers

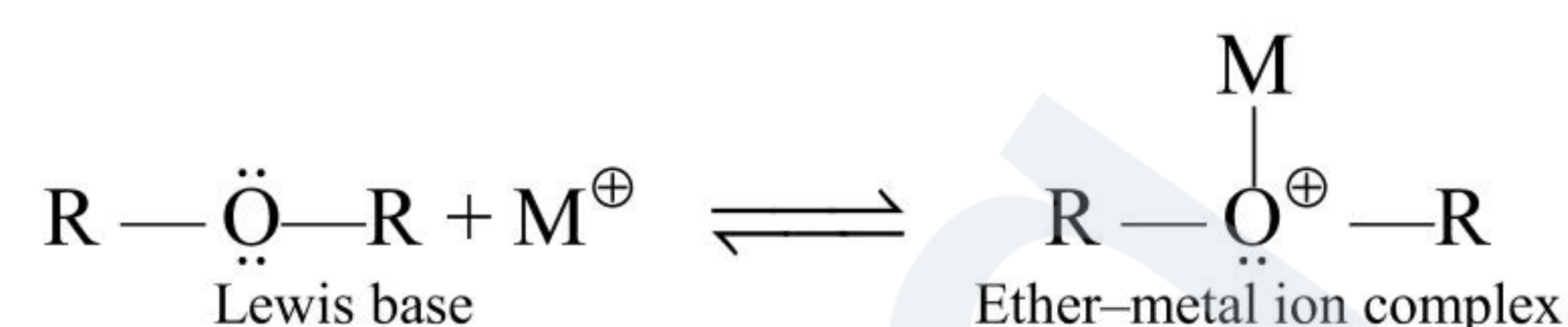
Crown ethers are heterocyclic polyethers with at least four oxygen atoms which have ($\text{—OCH}_2\text{CH}_2\text{—}$) as the repeating unit.

Naming of crown ethers: The first number in the name represents the total number of atoms (C and O) bonds and the second number represents the number of O atoms, e.g.,

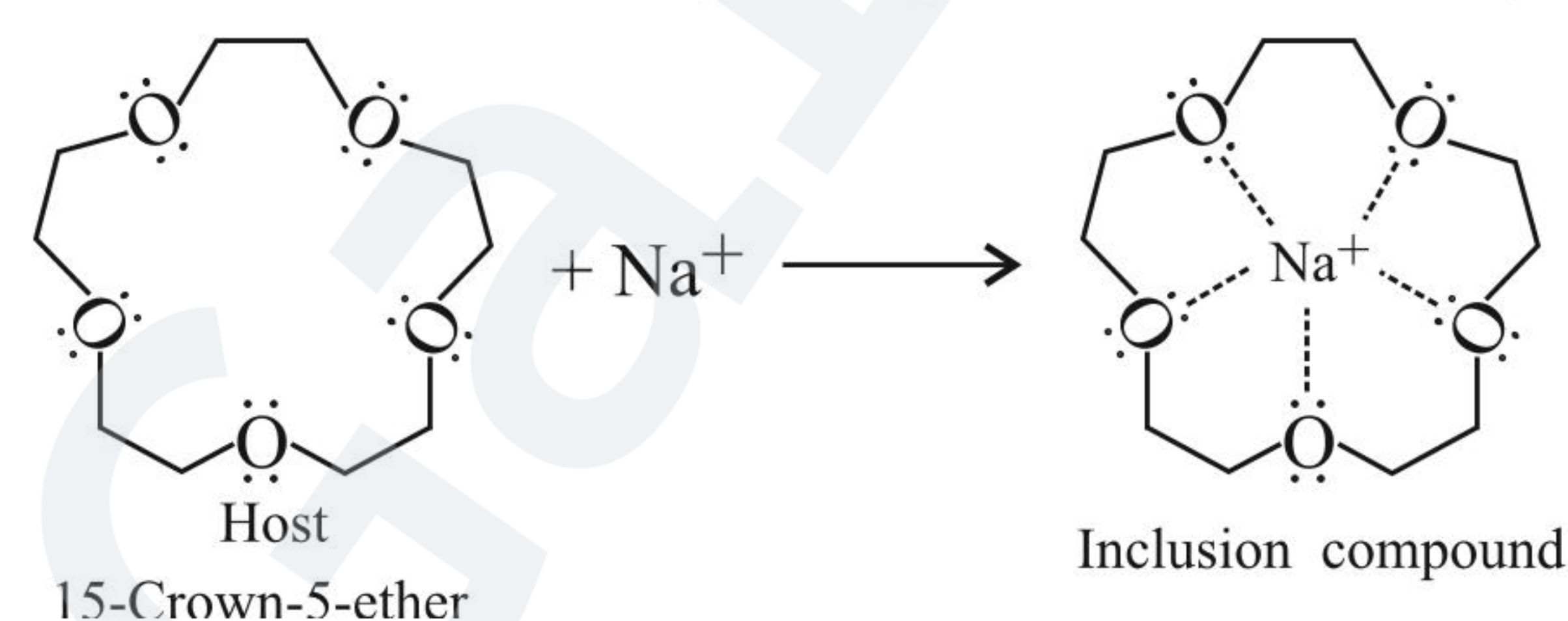


Crown ethers were given this name because their molecular models resemble crowns.

The polar nature of (C—O) bonds and the presence of unshared electron pairs on oxygen atom allow ethers to form complexes with metal ions.



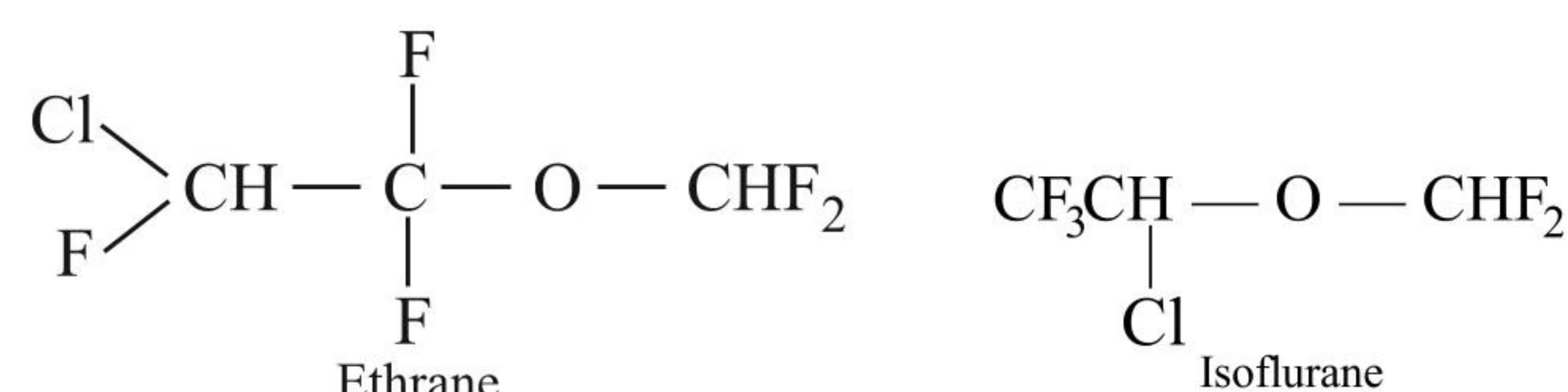
The strength of this oxygen-metal bond depends on the structure of ether. Crown ethers, a class of polyethers, is known to form more stable complexes with metal ions than simple ethers. A crown ether binds certain metal ions depending on the size of cavity.



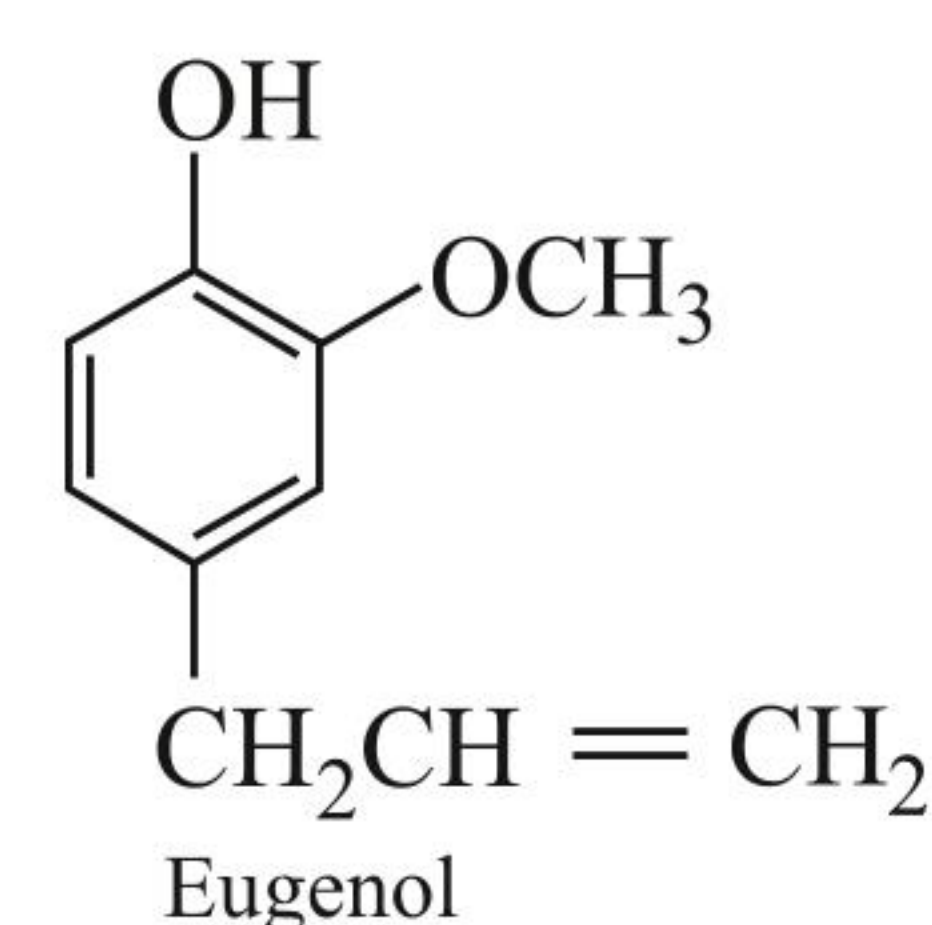
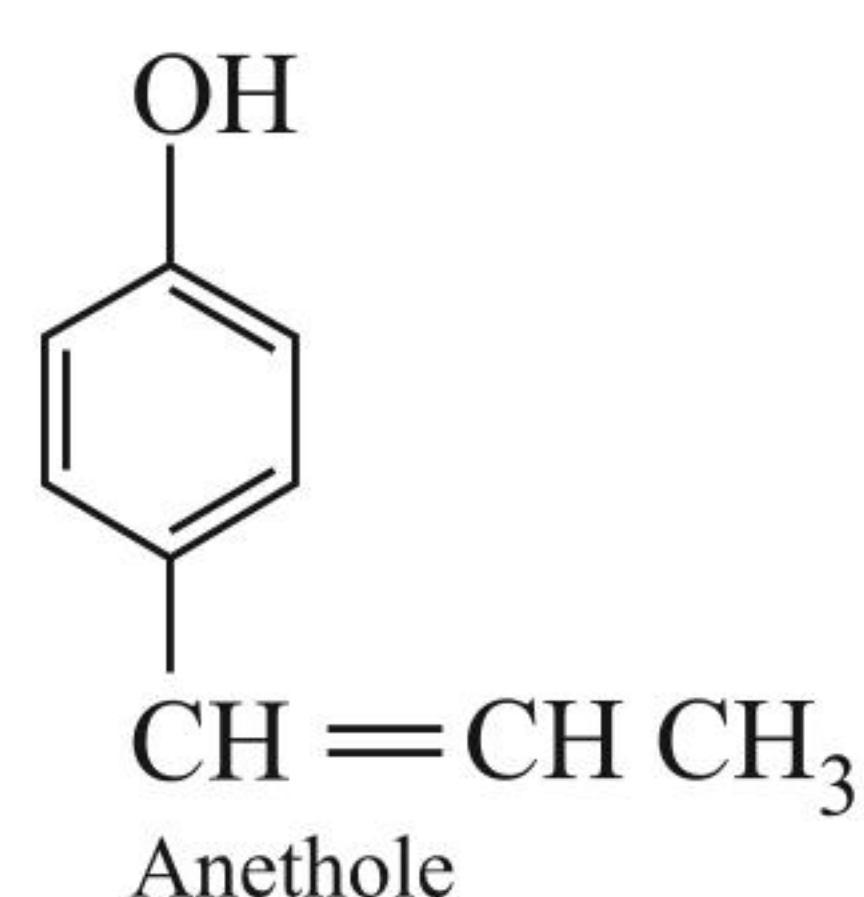
In this reaction, the crown ether is the 'host' and the species it binds is the 'guest'. The crown-guest complex is called an inclusion compound. Crown ethers allow inorganic salts to dissolve in non-polar solvents: for example, potassium ion of potassium permanganate forms a complex with the crown ether, thereby making KMnO_4 soluble.

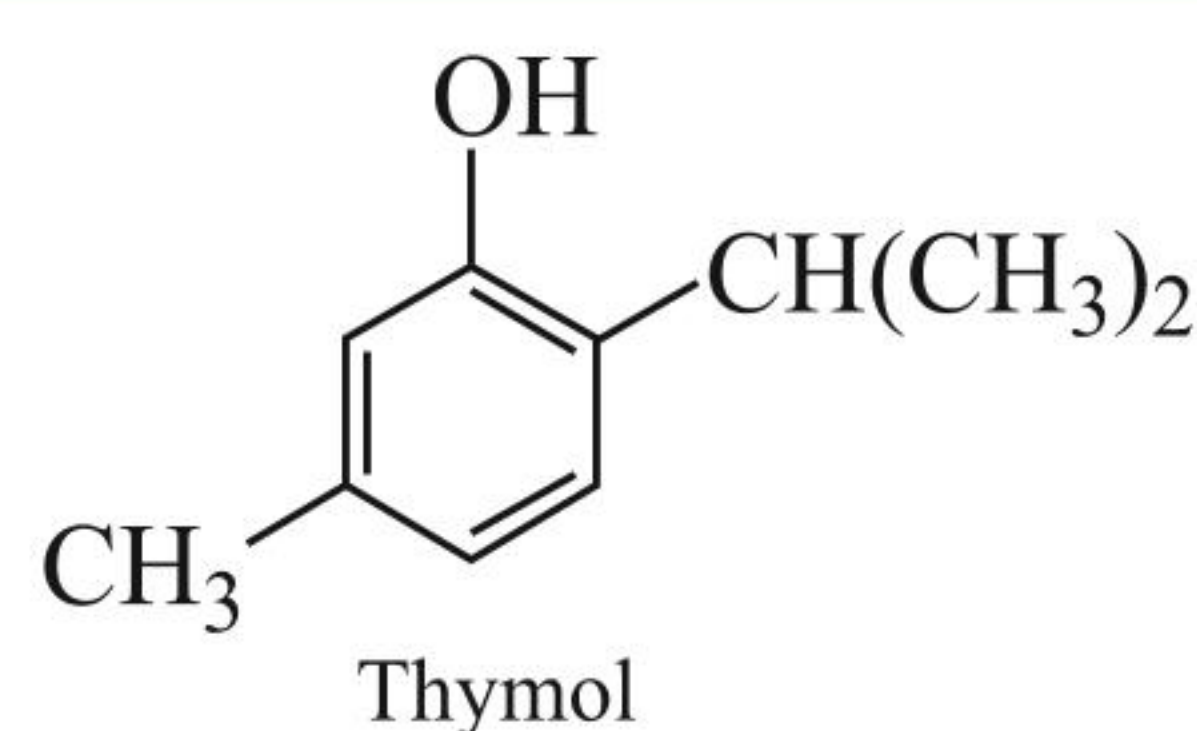
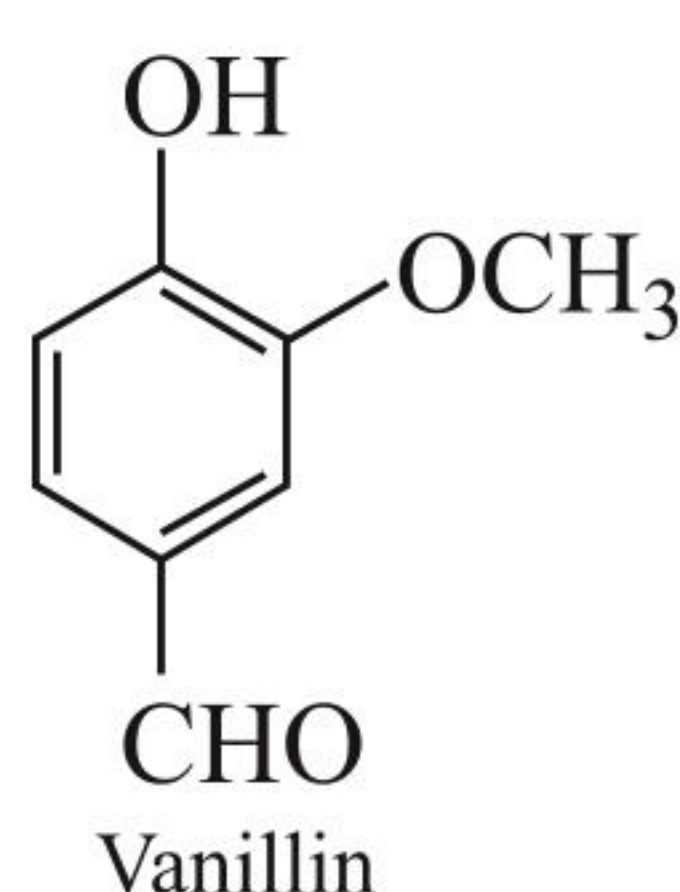
4.3.4 Uses of Ethers

The chemically unreactive nature, solvent properties, and low cost of ethoxy ethane make it the most important of simple ethers. It is used as a solvent for oils, gums resins, etc. Ethoxy ethane has also been widely used as an inhalation anaesthetic. However, due to its slow effect and unpleasant recovery period, other compounds such as ethrane and isoflurane have replaced ethoxy ethane as an anaesthetic. Phenyl ether, another simple ether, is used as a heat transfer medium because of its high boiling point, 531 K.



A number of naturally occurring phenols and ethers, particularly ring-substituted anisoles, are used as flavouring agents and in perfumes because of their pleasant odour. Anethole (a constituent of anise seed), eugenol (present in oil of cloves), vanillin (present in oil of vanilla bean), and thymol (present in thyme and mint) are examples of phenols and ethers used as perfumes and flavouring agents.





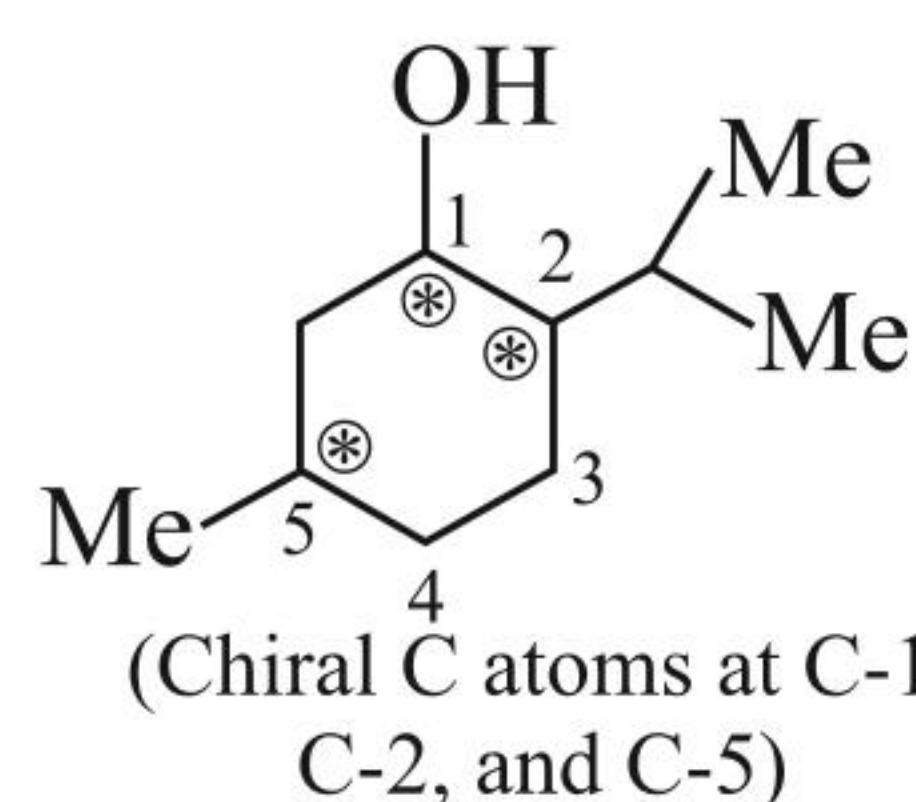
4.4 COMPARISON BETWEEN THE STRUCTURES OF ALCOHOLS, PHENOLS, AND ETHERS

S.No.	Compounds	Nature of hybridisation, bond angle, and bond length
1.	Methanol 	<p>a. 3 σ-bonds (C—H) \Rightarrow Formed by the overlap of sp^3 (C) — 1s (H)</p> <p>b. 1 σ-bond (C—O) \Rightarrow Overlap of sp^3 (C) — sp^3 (O)</p> <p>c. 1 σ-bond (O—H) \Rightarrow Overlap of sp^3 (O) — 1s (H)</p> <p>d. The bond angle $\left(\text{C} \text{---} \text{O} \text{---} \text{H} \right)$ is slightly less than the tetrahedral (T.H.) angle ($109^\circ, 28'$) due to repulsion between l.p.-l.p. (lone pair) of oxygen.</p>
2.	Phenol 	<p>a. 5 σ-bonds (C—H) in phenyl ring \Rightarrow Formed by the overlap of sp^2 (C)—1s (H)</p> <p>b. 3 σ-bonds in phenyl ring (C—C) \Rightarrow sp^2 (C)—sp^2 (C)</p> <p>c. 3 π-bonds in phenyl ring (C=C) \Rightarrow pure p (C)—pure p (C)</p> <p>d. 1 σ-bond (C—O) \Rightarrow sp^2 (C)—sp^3 (O)</p> <p>e. 1 σ-bond (O—H) \Rightarrow sp^3 (O)—1s (H)</p> <p>f. (C—O) bond in phenol is slightly less than that in methanol due to partial double bond character on account of the resonance of l.p. (lone pair) \bar{e}'s of O atom with the aromatic ring and (ii) sp^2 hybrid C atom to which the O atom is attached.</p>
3.	Methoxy methane 	<p>a. 6 σ-bonds (C—H) \Rightarrow Formed by the overlap of sp^3 (C)—1s (H)</p> <p>b. 2 σ-bonds (C—O) \Rightarrow sp^3 (C) — sp^3 (O)</p> <p>c. The bond angle $\left(\text{R} \text{---} \text{O} \text{---} \text{R} \right)$ is slightly greater than T.H. angle ($109^\circ, 28'$) due to repulsion between two bulky alkyl groups.</p> <p>d. (C—O) bond length is almost the same as in alcohols.</p>

ILLUSTRATION 4.1

- Write all the stereoisomers of 2-isopropyl-5-methylcyclohexanol and give the decreasing order of their stabilities.
- Write all the stereoisomers of 4-ethylcyclohexan-1,2-diol. Which is the most stable isomer?

Sol. a.



There are three chiral C atoms and there are four diastereomers, each with a pair of enantiomers. Thus total stereoisomers are 8.

<p>(I)</p>	<p>(II)</p>	<p>(III)</p>	<p>(IV)</p>
$\left(\begin{array}{l} \text{OH} \Rightarrow \text{e}, \text{i-Pr} \Rightarrow \text{e} \\ \text{Me} \Rightarrow \text{e} \end{array} \right)$ All equatorial (most stable) Three (e)	$\left(\begin{array}{l} \text{OH} \Rightarrow \text{a}, \text{i-Pr} \Rightarrow \text{e} \\ \text{Me} \Rightarrow \text{e} \end{array} \right)$ Two (e) Me is bulky, so in e-position; more stable	$\left(\begin{array}{l} \text{OH} \Rightarrow \text{e}, \text{i-Pr} \Rightarrow \text{e} \\ \text{Me} \Rightarrow \text{a} \end{array} \right)$ Two (e) Me is in (a)-position, so less stable	$\left(\begin{array}{l} \text{OH} \Rightarrow \text{a}, \\ \text{i-Pr} \Rightarrow \text{e} \\ \text{Me} \Rightarrow \text{a} \end{array} \right)$ One (e) least stable

Commercially, absolute alcohol is prepared by azeotropic distillation method. Rectified spirit is mixed with a suitable amount of benzene and subjected to fractional distillation. The first fraction obtained at 331.8 K is the tertiary azeotrope

consisting of H_2O , some alcohol, and benzene (H_2O : benzene : alcohol : : 7.4% : 74.1% : 18.5%).

The second fraction, a binary azeotrope consisting of all the remaining benzene and some alcohol (benzene : alcohol : : 67.7% : 32.2%), then distills over at 341.2 K. Absolute alcohol, boiling point 351 K, is obtained as the last fraction.

- f. Power alcohol:** Alcohol used for generating power is called power alcohol (absolute alcohol : petrol : : 20 : 80). Benzene, ether, or tetralin is added as a cosolvent.
- g. Methylated spirit or denatured alcohol:** The alcohol is denatured by the addition of poisonous substances such as CH_3OH , acetone or pyridine, and some colouring matter such as CuSO_4 . Such a sample of alcohol is called methylated spirit or denatured alcohol.

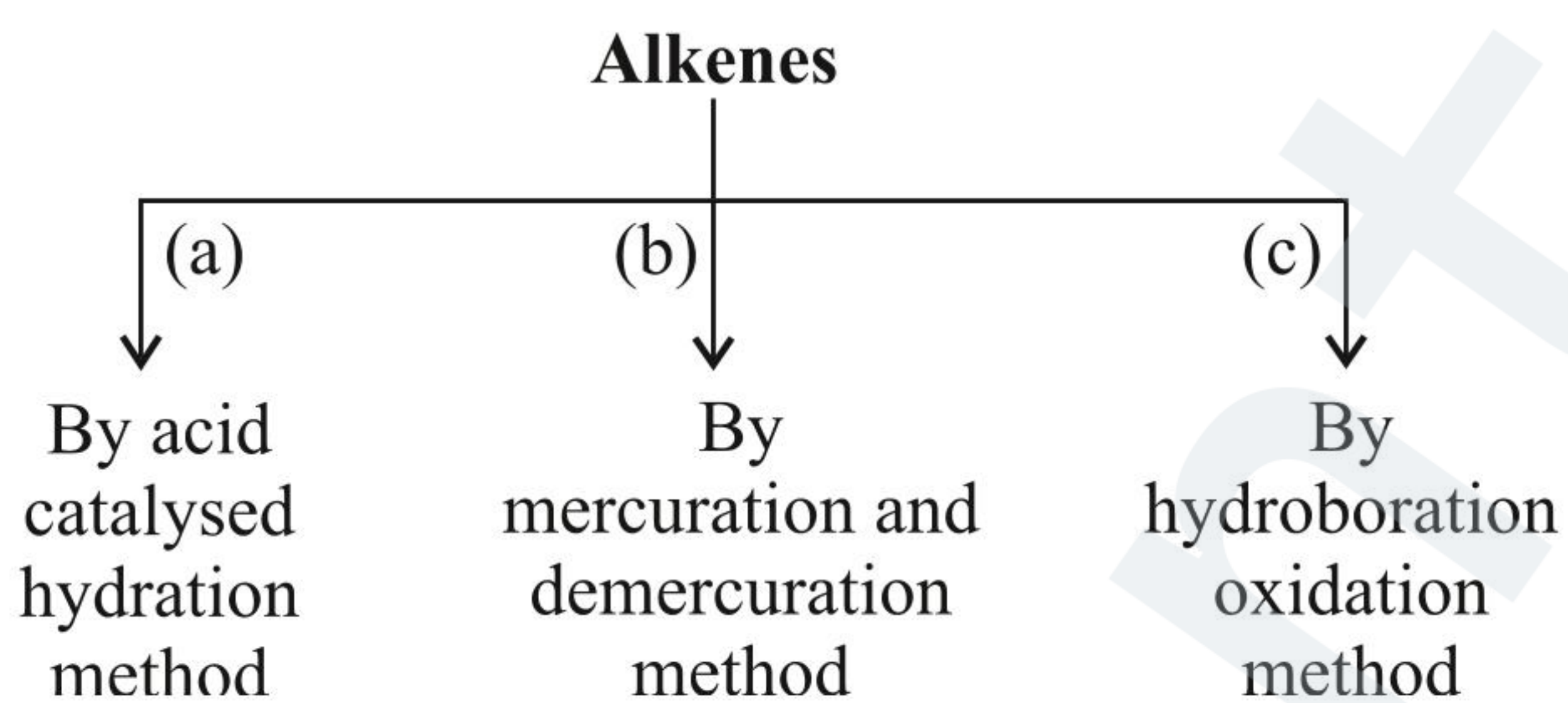
4.6.1 ALCOHOLIC PROOF

It is used to describe the alcohol contents of wines and beer. Proof is defined as twice the percentage by volume of alcohol in an ethanol- H_2O mixture. Thus, a wine with 10% by volume is 20 proof and a 70 proof alcoholic liquor means it has 35% ethanol.

4.7 PREPARATION OF ALCOHOLS

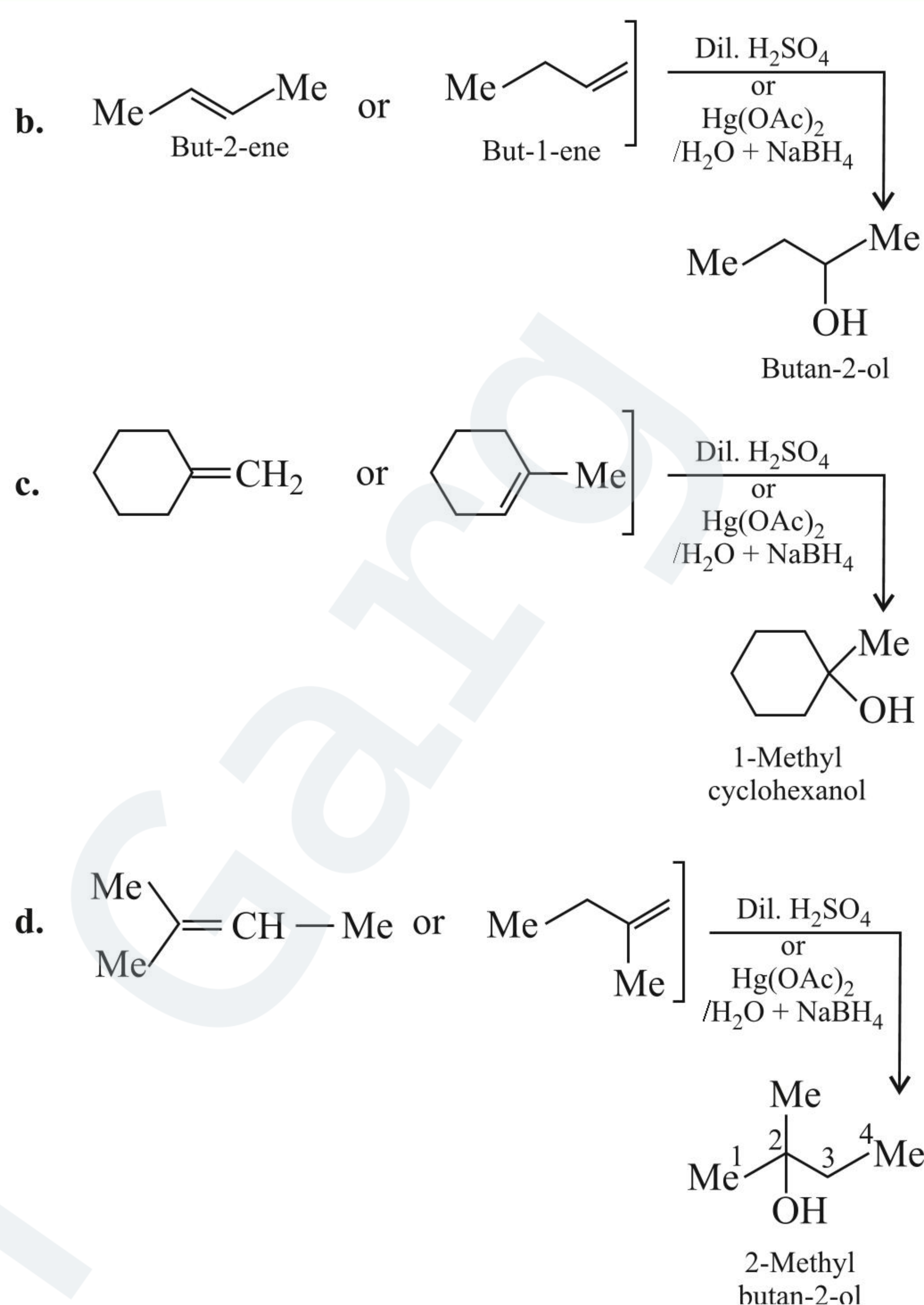
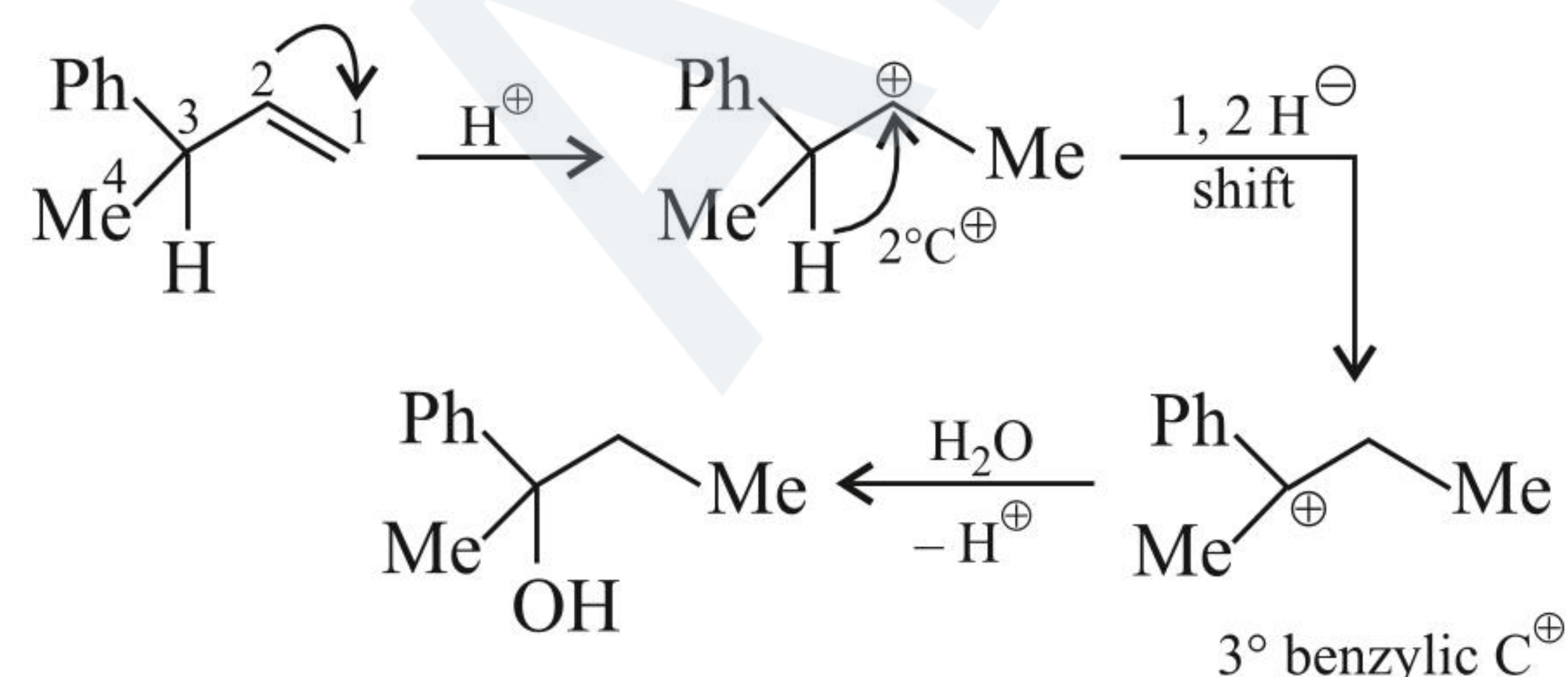
From Alkenes

Alcohols are prepared from alkenes by the following methods:

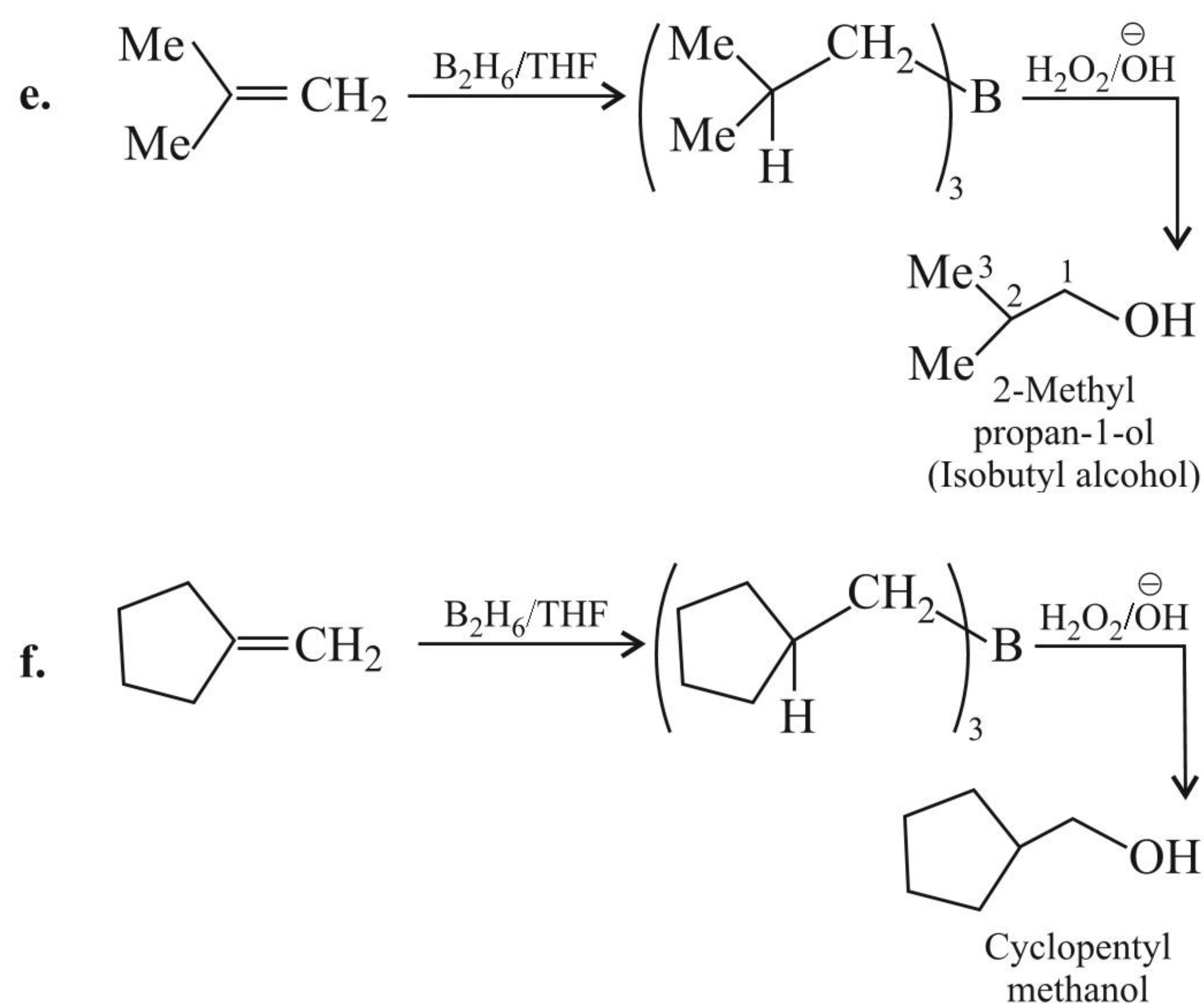


4.7.1 SOME EXAMPLES

- a.** Hydration of 3-phenyl but-1-ene in dil. H_2SO_4 is not a satisfactory method for preparing 3-phenyl butan-2-ol but 2-phenyl-butan-2-ol is obtained. Ph shift is better than H^\ominus shift, yet $1,2\text{-H}^\ominus$ shift occurs leading to a more stable 3° benzylic C^\ominus .

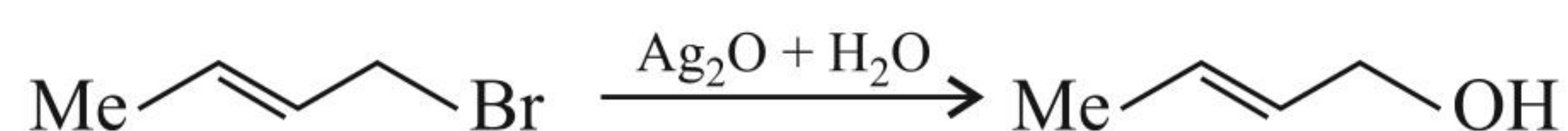


In (b), (c), and (d) in both catalytic hydration and mercuration demercuration reaction, addition takes place by Markovnikov's rule.



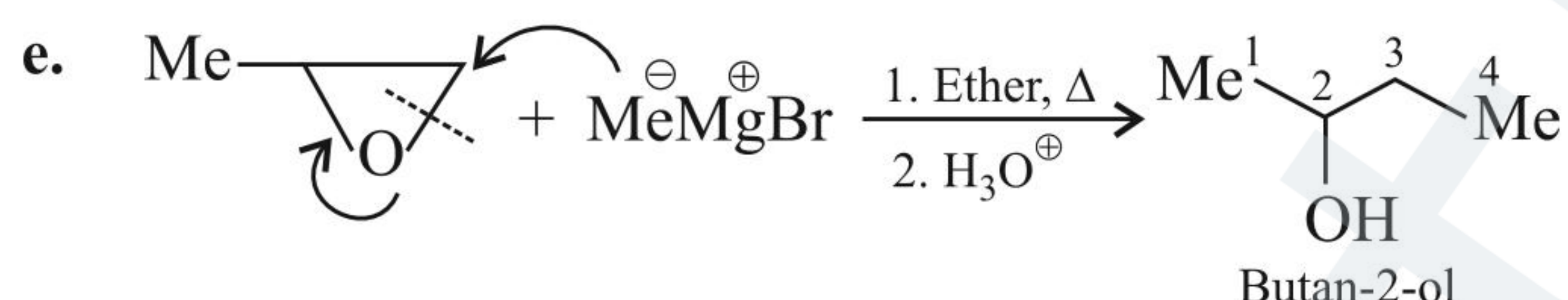
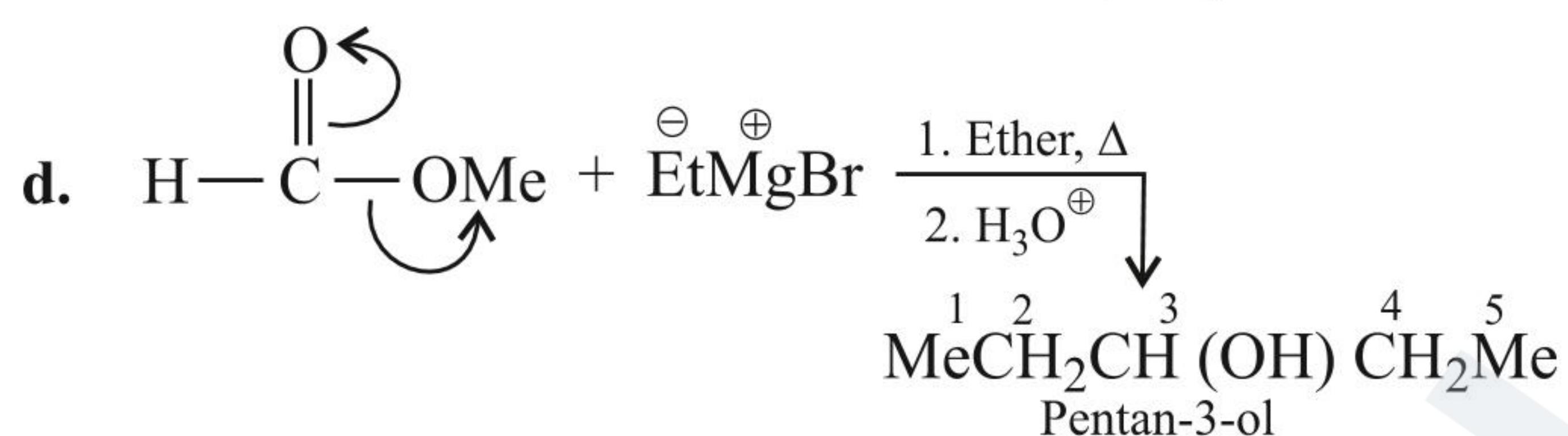
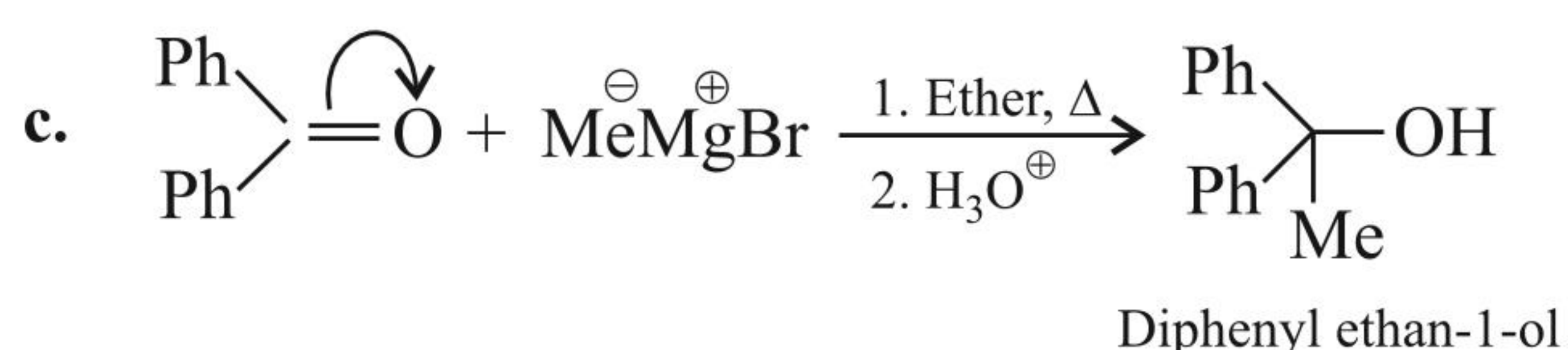
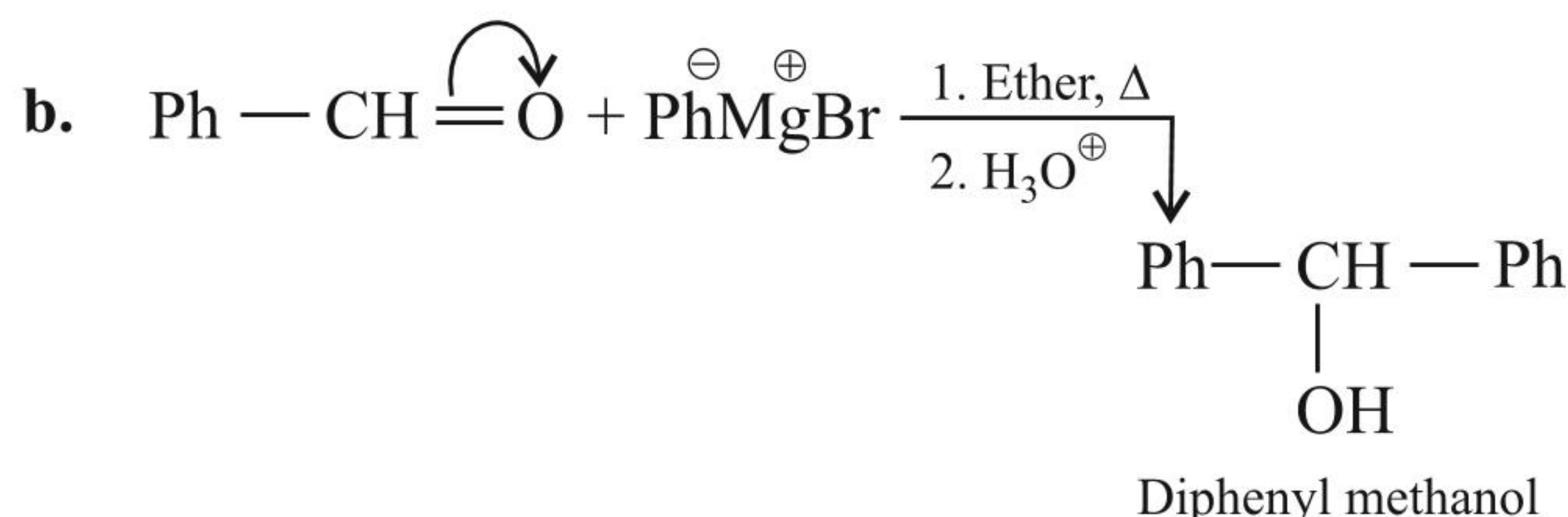
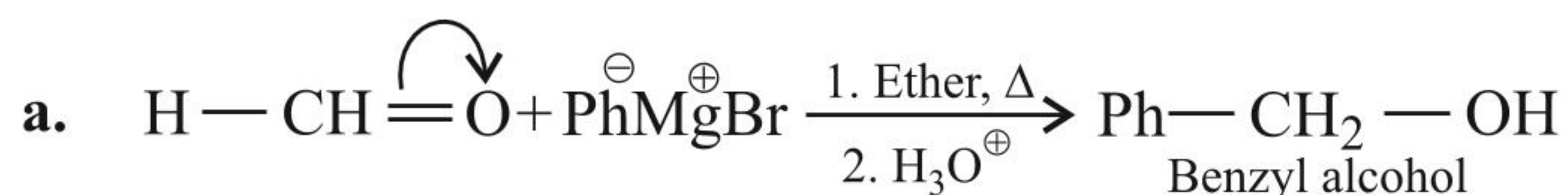
In (e) and (f), the addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp^2 C atom with greater number of H atoms, i.e., alcohol is formed by the addition of H_2O by anti-Markovnikov's rule.

4.7.2 FROM ALKYL HALIDE WITH Ag_2O IN H_2O



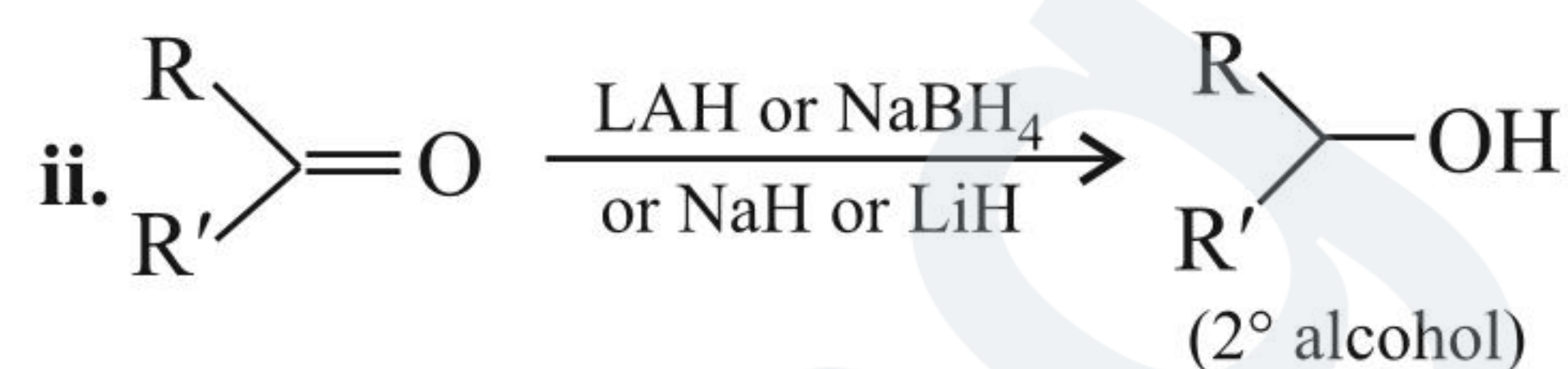
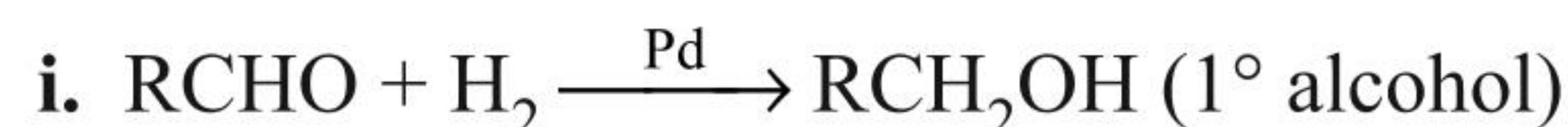
4.7.3 FROM GRIGNARD REAGENTS (G.R.)

Alcohols are produced by reacting G.R. with aldehydes, ketones, esters epoxides (cyclic ethers), O_2 , etc.



4.7.4 FROM CARBONYL COMPOUNDS

a. Aldehydes and ketones are reduced to alcohols by catalytic hydrogenation (finely divided metal, Pt, Ni, or Pd) and with NaBH_4 , LAH, NaH, or LiH.



b. Reduction of acids and esters:

Carboxylic acids are reduced to 1° ROH in excellent yield by LAH (strong reducing agent), since LAH is an expensive reagent, therefore, acids are reduced to 1° ROH by converting them to the esters followed by their reduction by catalytic hydrogenation.

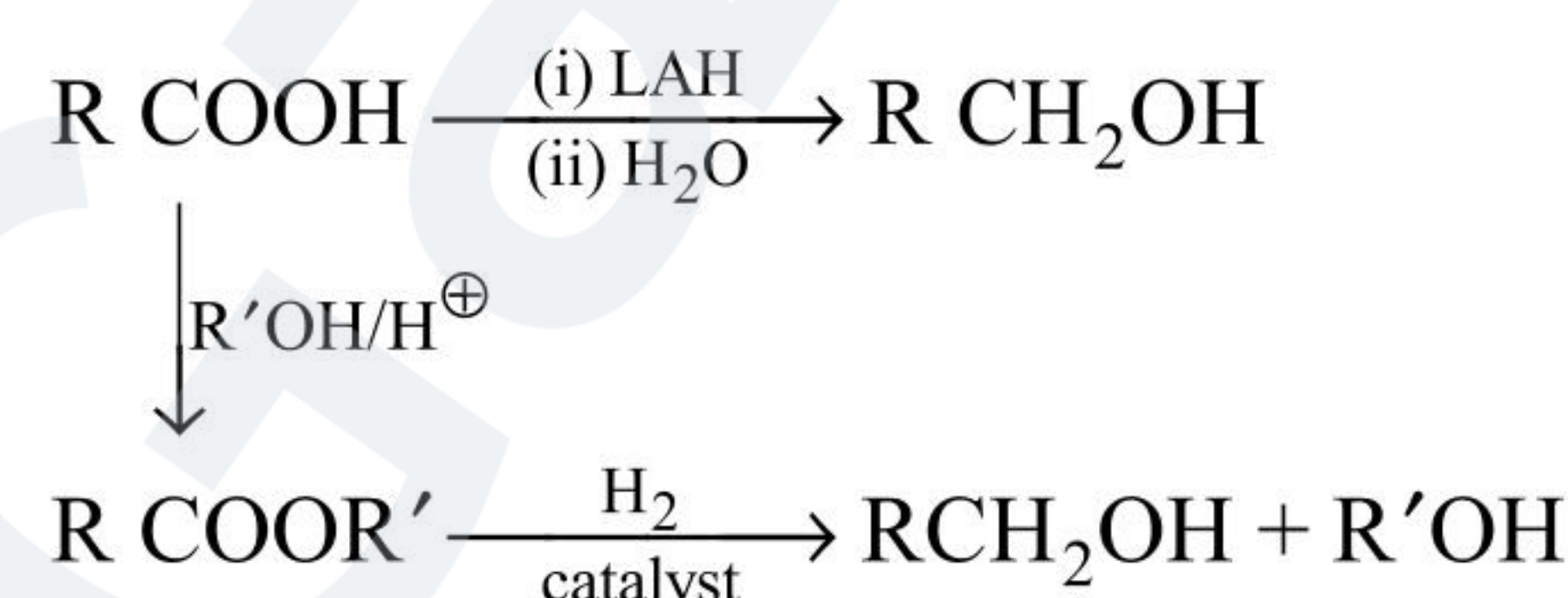
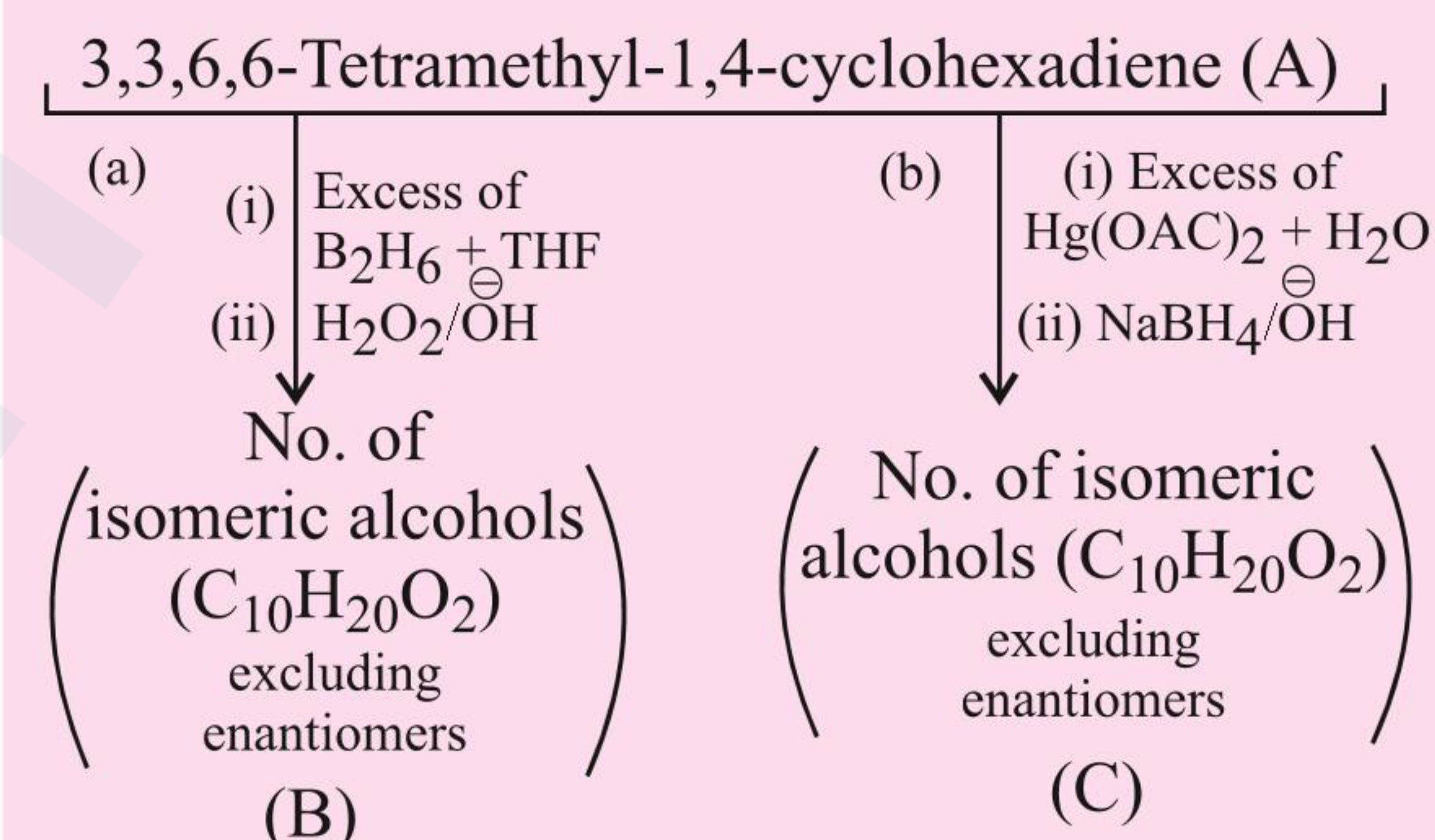
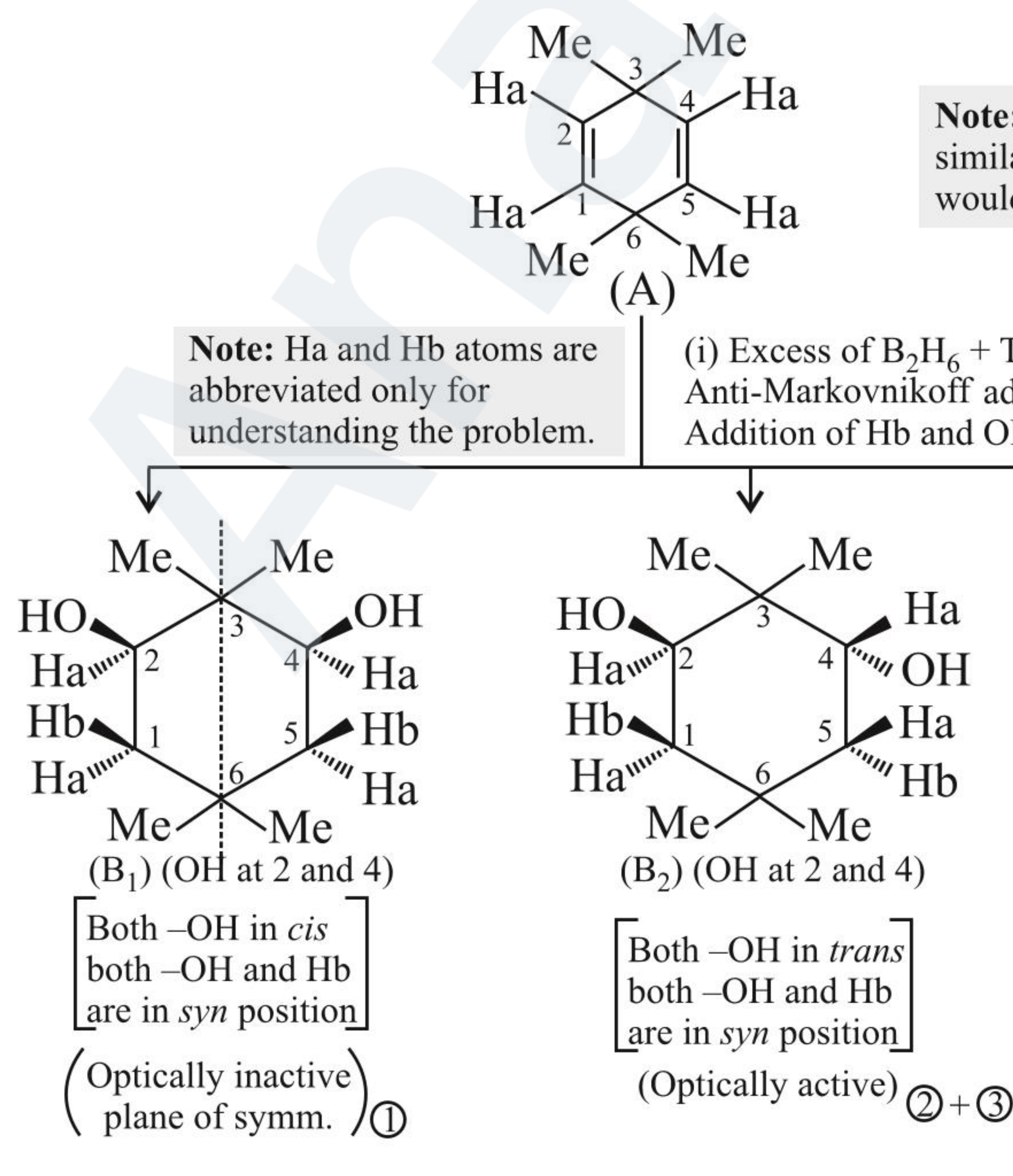


ILLUSTRATION 4.2



What are the numerical values of (B) and (C)?

Sol. a. (4)

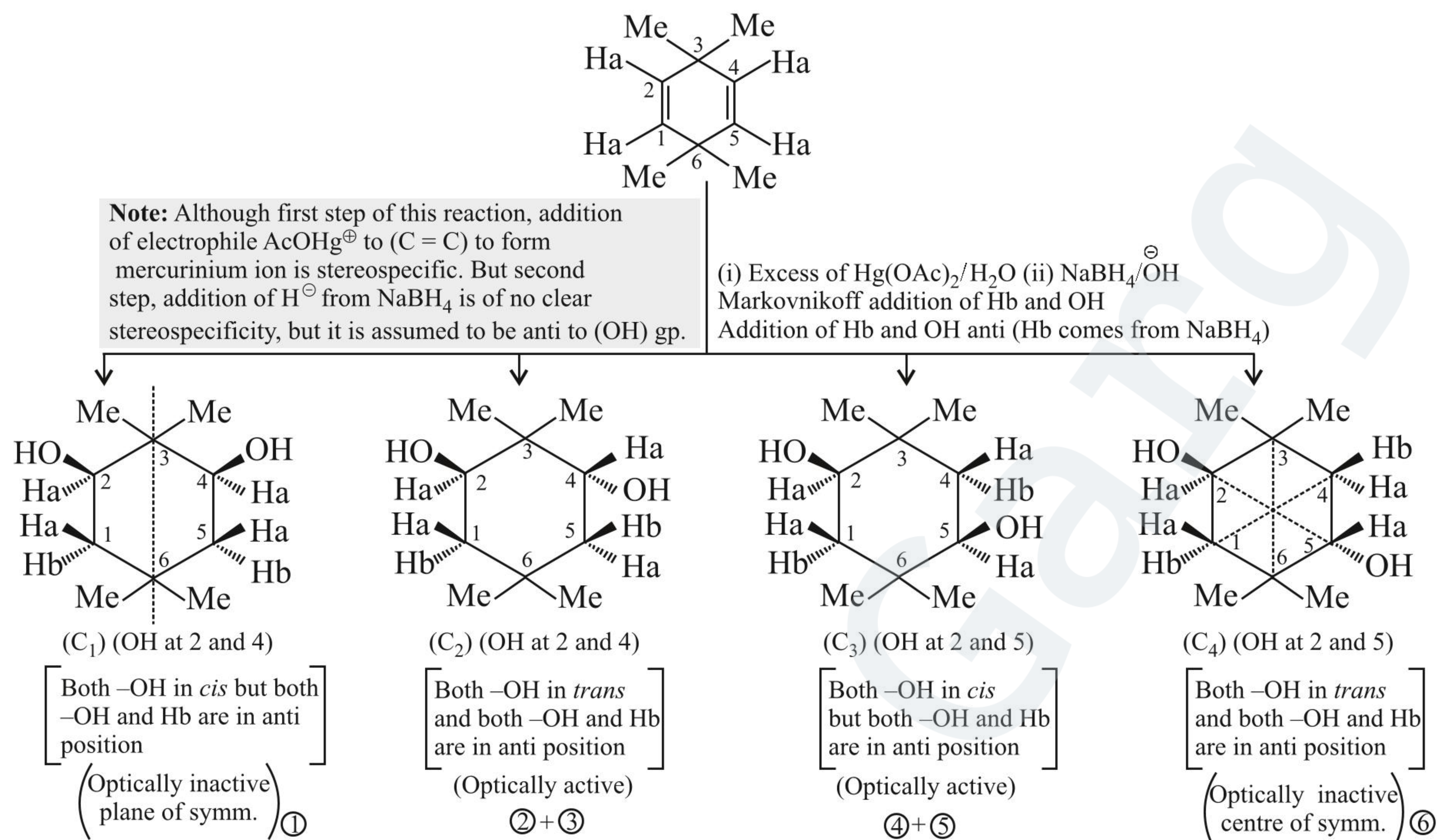


Note: Positions 1, 2, 4, and 5 are similar: reaction at 1 or 2 and at 4 or 5 would give same product.

Thus, the number of isomers excluding enantiomers is 4.

The number of isomer including stereoisomers = ⑥

b. (4)



Thus, the number of isomers excluding enantiomers is 4.

The number of isomers including stereoisomer = 6.

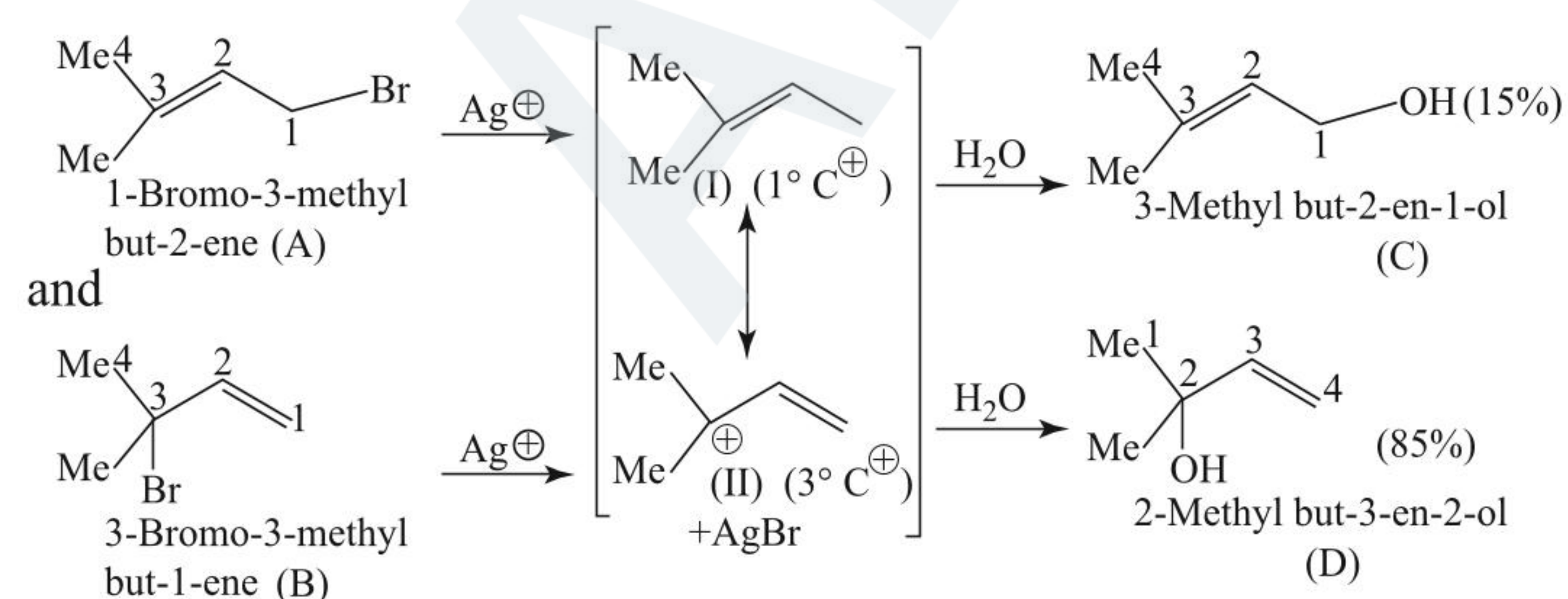
Note: The products B₁ and C₁, B₂ and C₂, B₃ and C₃, B₄ and C₄ are same.

If the reaction (a) is carried out with excess of $\text{B}_2\text{D}_6 + \text{THF} + \text{H}_2\text{O}_2/\text{OH}^-$ and (b) is carried out with excess of $\text{Hg}(\text{OAc})_2 + \text{H}_2\text{O} + \text{NaBD}_4$, then in place of Hb , D will come in all product, and the products B₁ and C₁, B₂ and C₂, B₃ and C₃, and B₄ and C₄ would be different.

4.7.5 OXYMERCURATION-DEMERCURATION (OMDM) REACTION FOR THE PREPARATION OF ALCOHOLS AND HYDROBORATION OXIDATION FOR THE PREPARATION OF ALCOHOL

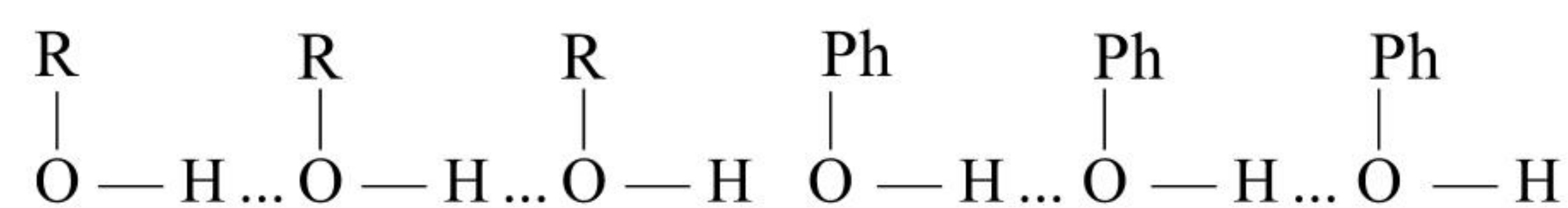
Oxymercuration-demercuration reaction and hydroboration oxidation for the preparation of alcohol are already discussed in Chapter 7 (Part 1).

4.7.6 TREATING HALOALKENE WITH MOIST Ag_2O OR $(\text{AgCl} + \text{H}_2\text{O})$ TO GIVE ALCOHOL



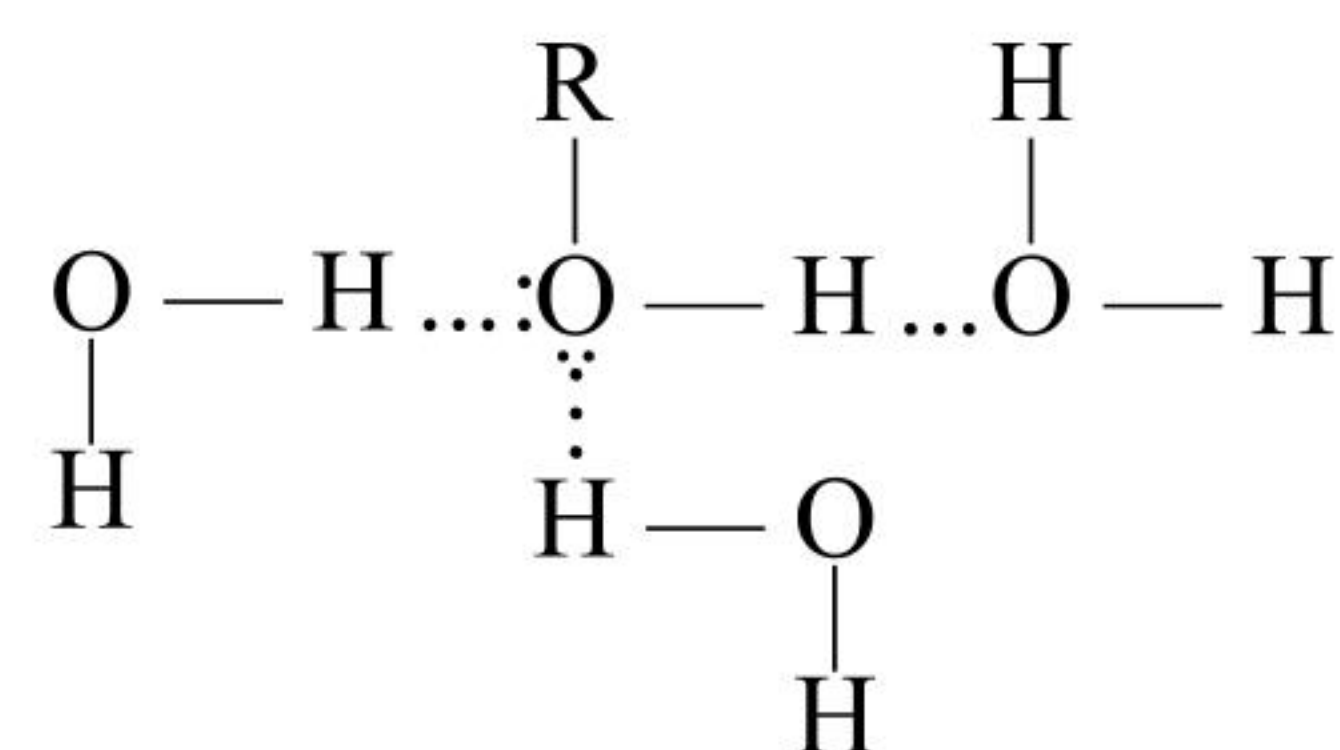
4.8 PHYSICAL PROPERTIES

a. Boiling points: The boiling points of alcohols and phenols increase with the increase in C atoms due to the increase in van der Waals forces and decrease with increase in branching of C-chain due to decrease in surface area. They are also involved in intermolecular H-bonding. As a result the boiling points of alcohols and phenols are higher in comparison to hydrocarbons, RX , ArX , ethers of comparable molecular masses.



Thus b.p.'s of $\text{C}_2\text{H}_5\text{OH} > \text{Me}-\text{O}-\text{Me} > \text{MeCH}_2\text{Me}$
 B.P.: 351 K 248 K 231 K
 Molecular mass: 46 46 44.

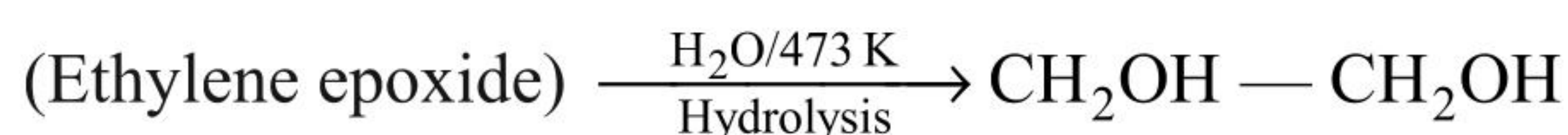
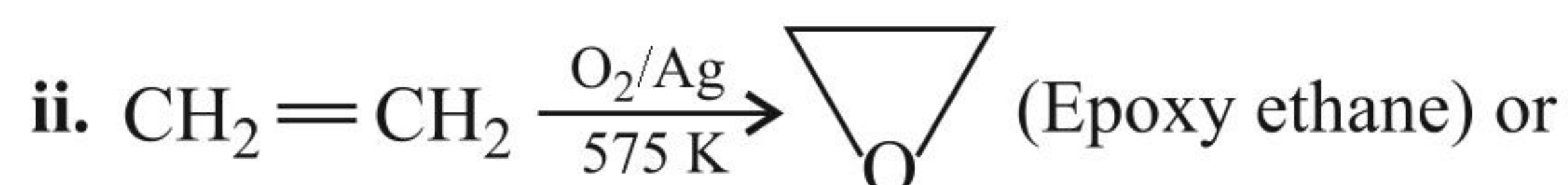
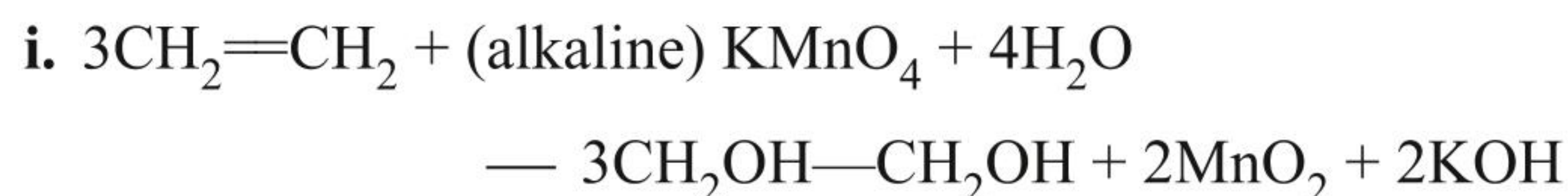
b. Solubility: Solubilities of alcohols and phenols in water is due to formation of H-bonds with H_2O . The solubility increases with decrease in size of $\text{R}-$ or Ar (hydrophobic part).



4.9 DIHYDRIC ALCOHOLS

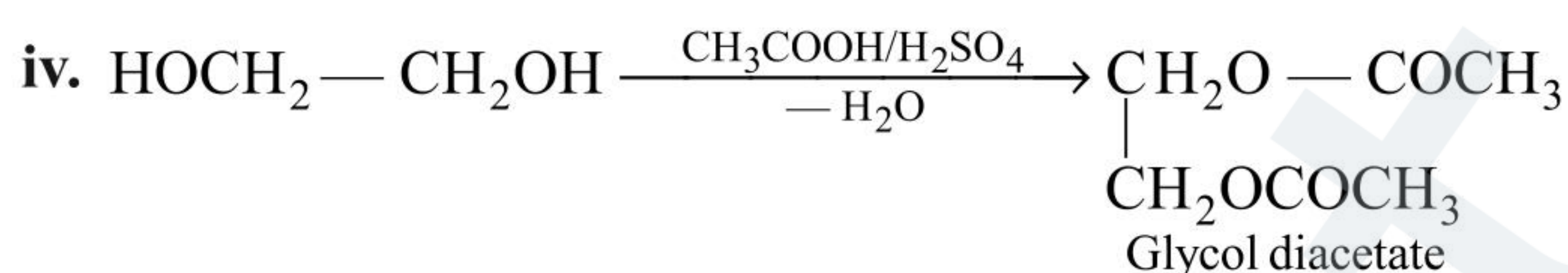
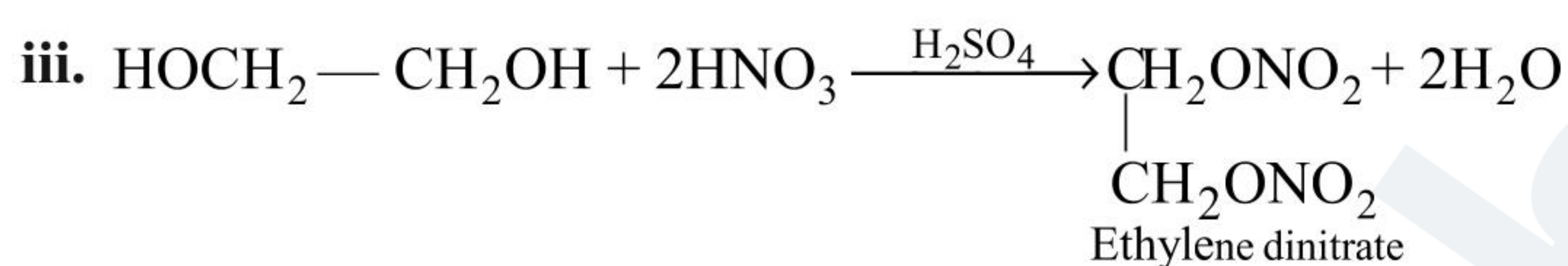
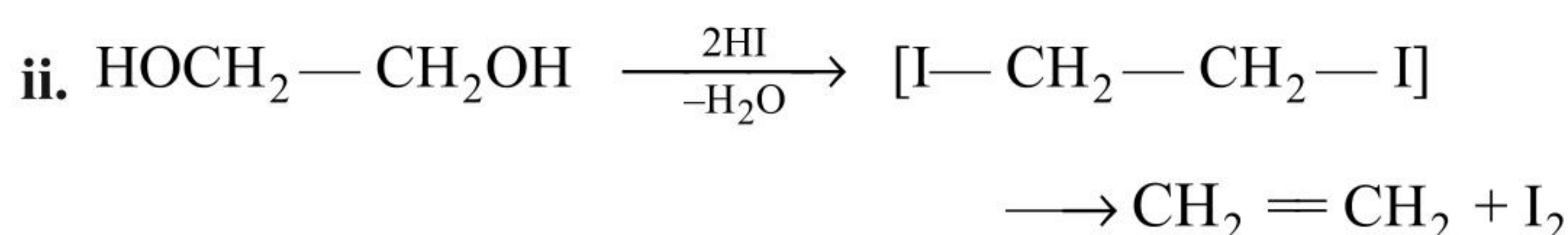
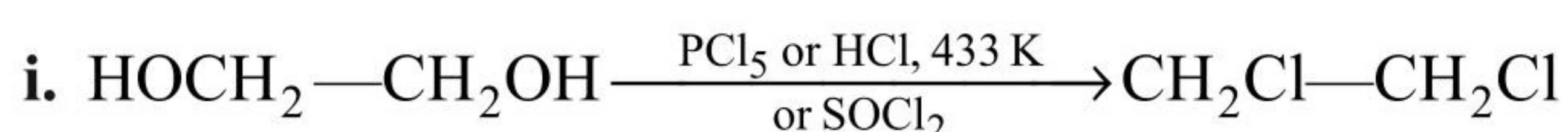
4.9.1 ETHYLENE GLYCOL OR ETHANE-1,2-DIOL

a. Preparation:

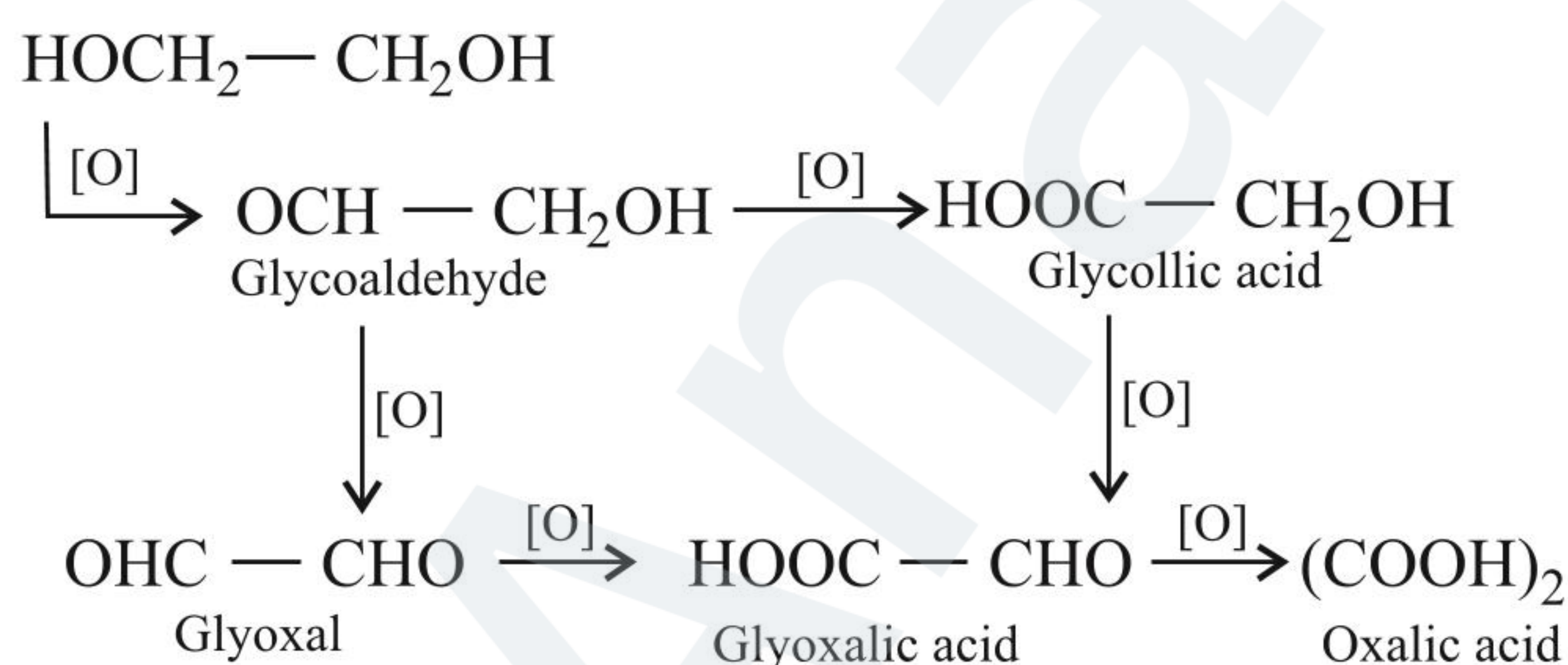


Ethylene glycol undergoes extensive intermolecular H-bonding. As a result, dihydric alcohols are highly associated and have high boiling point, high viscosity, and are highly soluble in H_2O .

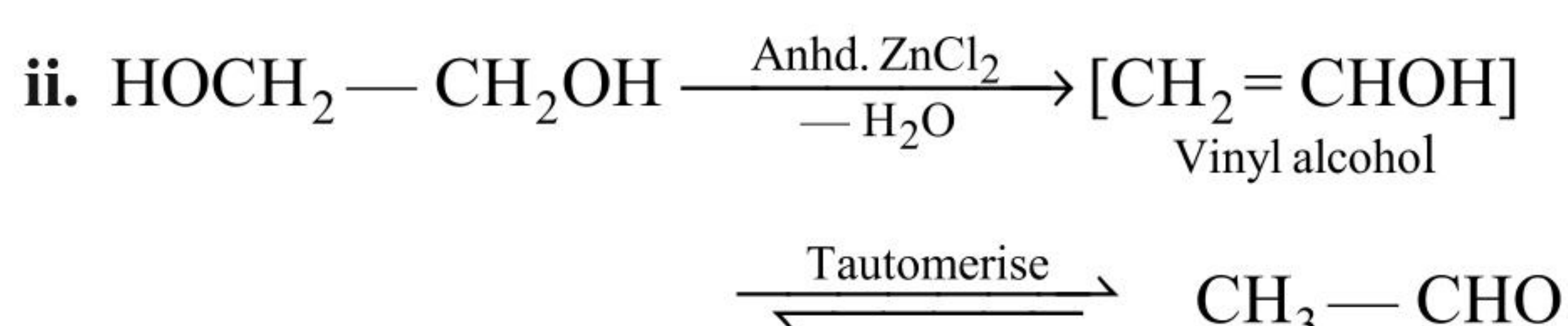
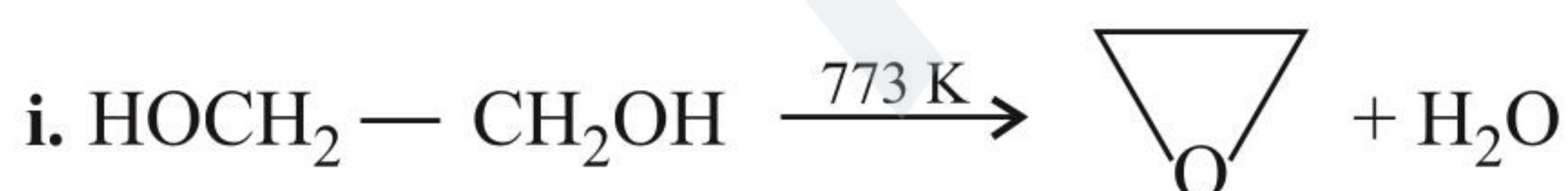
b. Reactions:



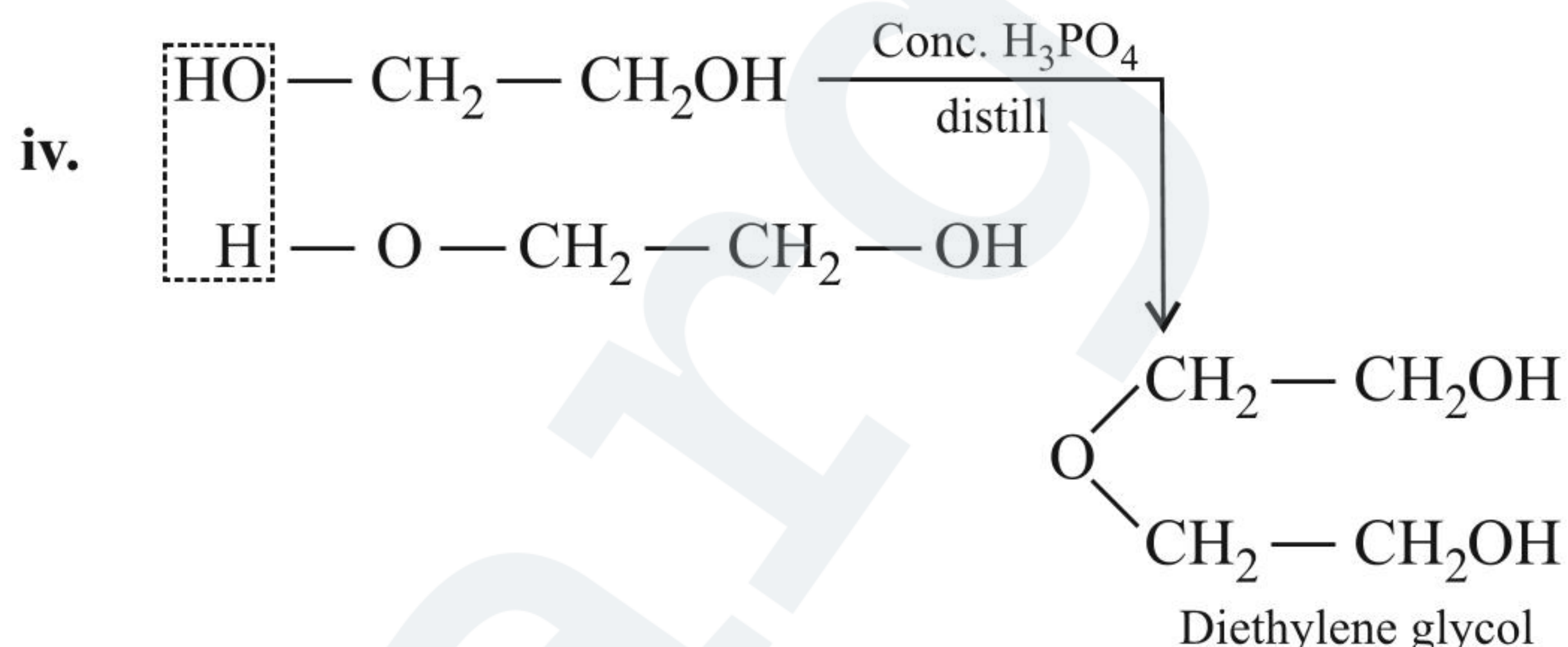
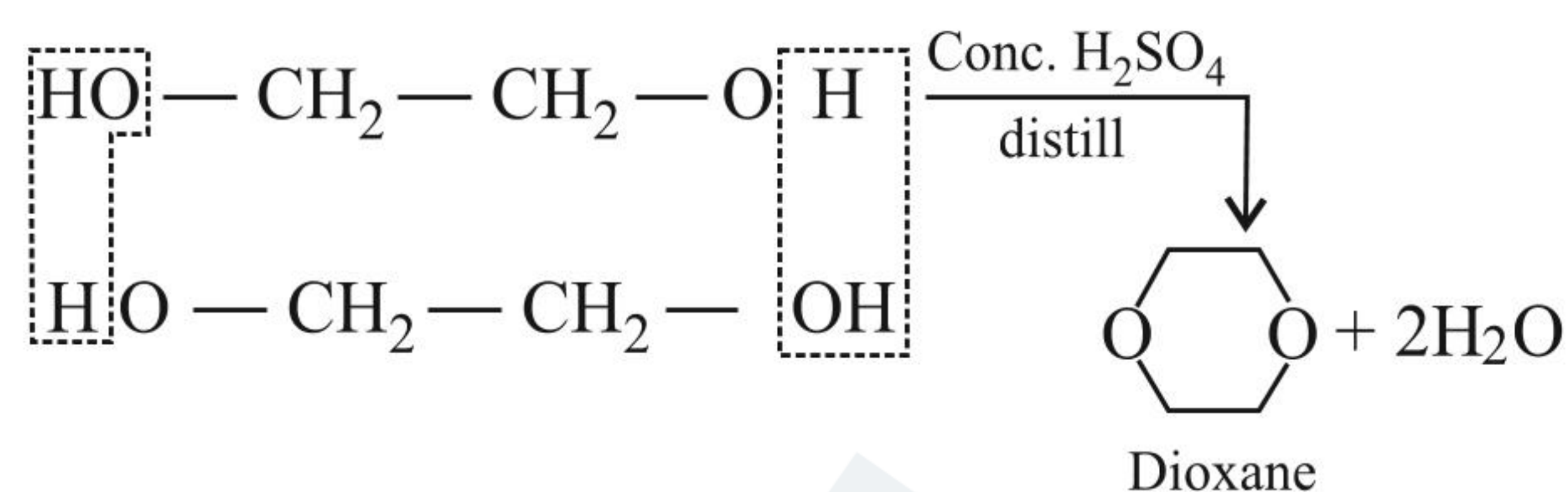
c. Oxidation: Ethylene glycol on oxidation with conc. HNO_3 mainly gives glycollic acid and oxalic acid. The other oxidation products such as glyoxal and glyoxalic acid are also formed in small quantities because they are more readily oxidised than glycol itself.



d. Dehydration:

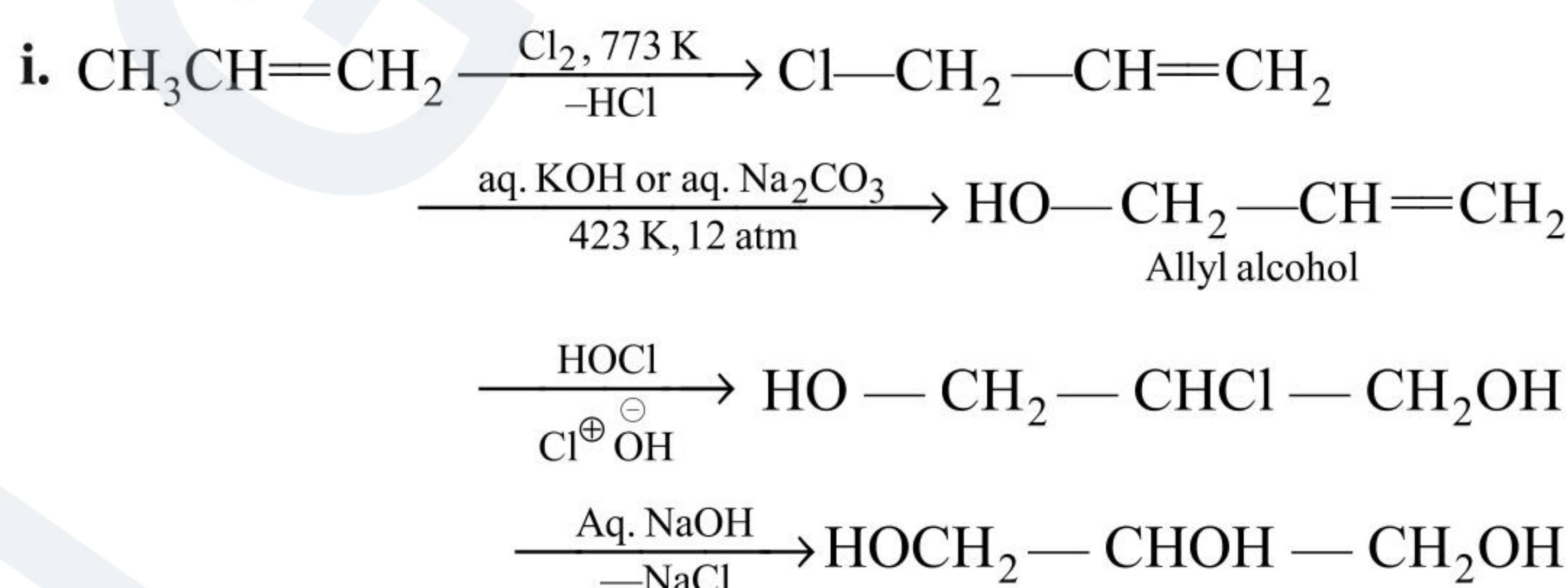


iii. With conc. H_2SO_4 :



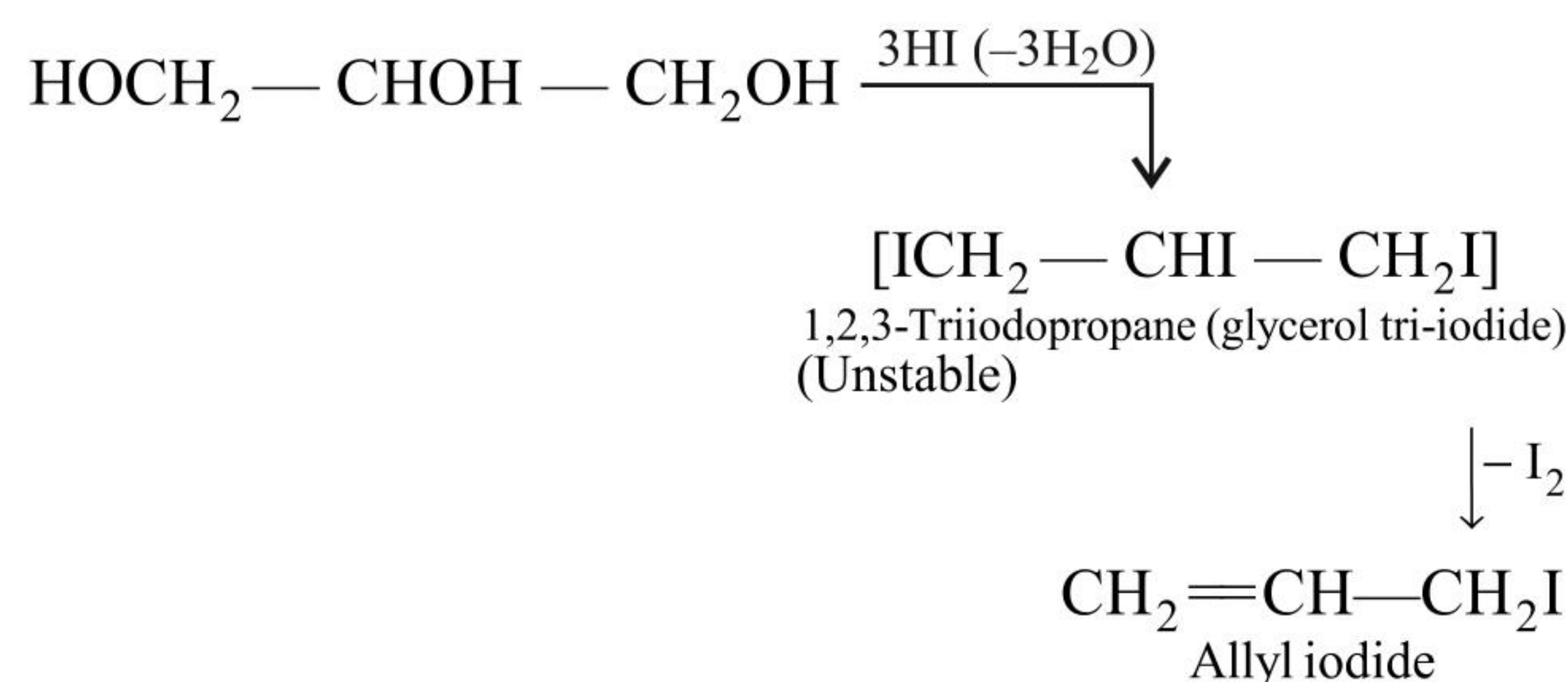
4.9.2 TRIHYDRIC ALCOHOLS: GLYCEROL OR GLYCERINE 1,2,3-PROPANETRIOL

a. Preparation:

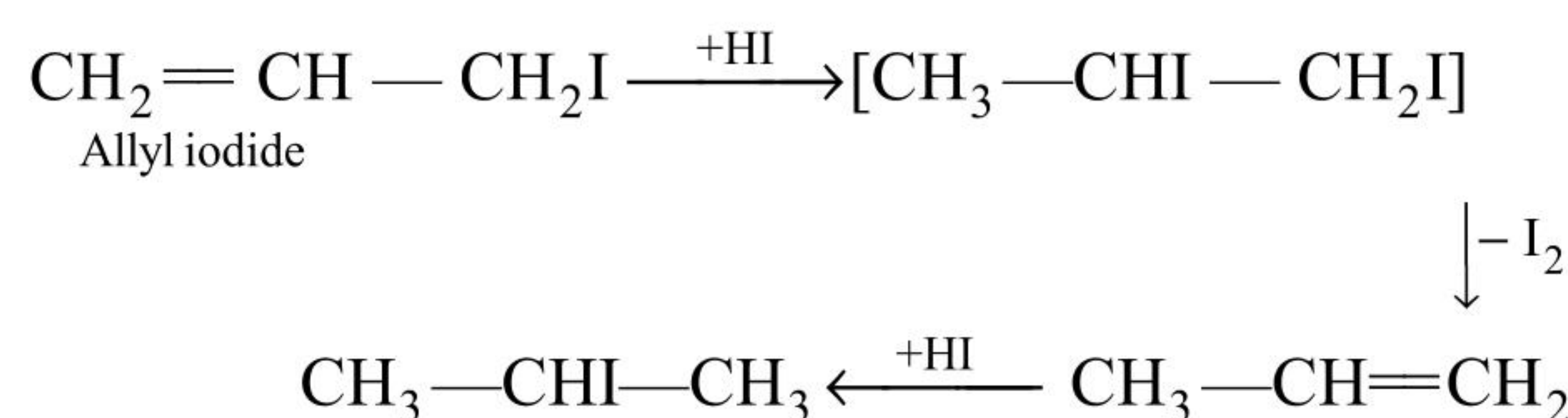


b. Properties: Due to the presence of three ($-\text{OH}$) groups, it undergoes extensive intermolecular H-bonding, and thus it has high boiling point, high viscosity, and is highly soluble in H_2O .

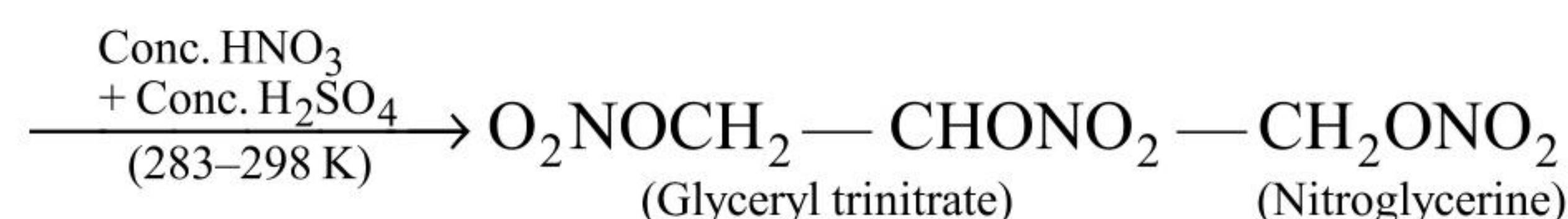
c. Reaction: When glycerol is treated with a small amount of HI or PI_3 , allyl iodide is formed.



When a large amount of HI is used, the main product is isopropyl iodide.

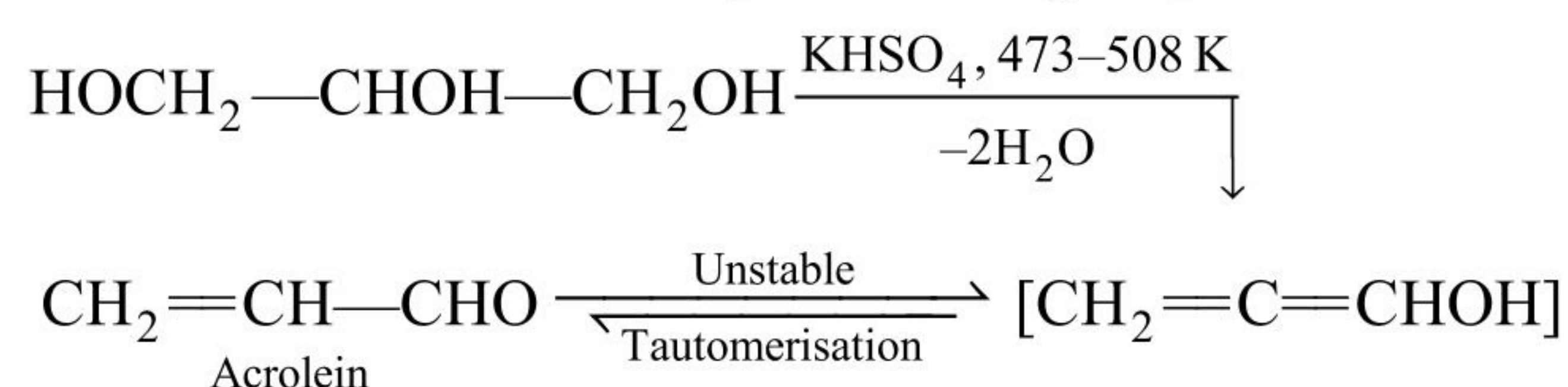


d. Nitration: $\text{HOCH}_2-\text{CHOH}-\text{CH}_2\text{OH}$

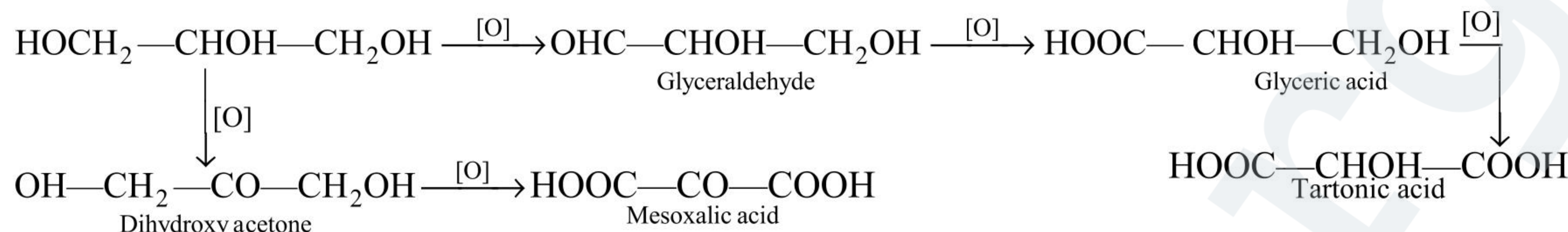


A mixture of glycerol trinitrate and glyceryl dinitrate adsorbed on Kieselguhr is called **dynamite**, discovered by Alfred Nobel.

e. Dehydration with KHSO_4 or conc. H_2SO_4 :

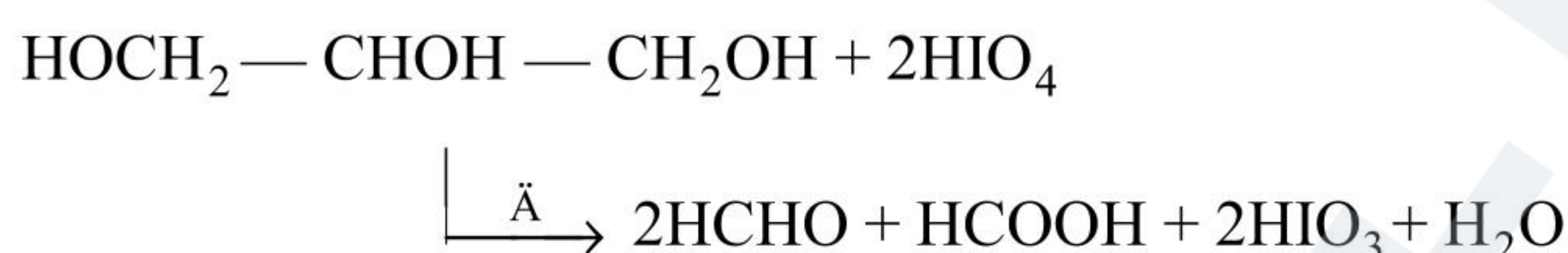


f. Oxidation:

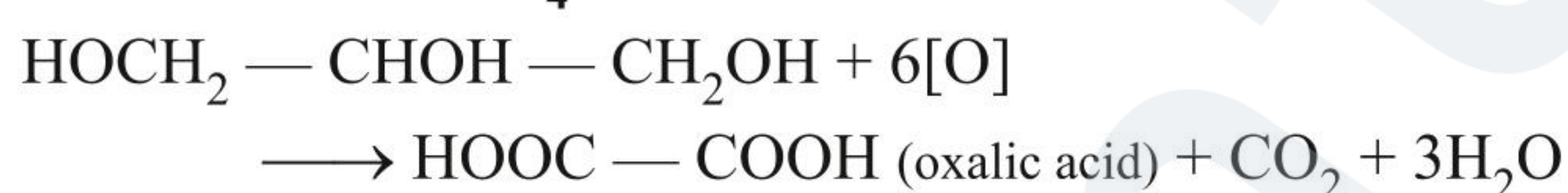


- i. With dil. HNO_3 , a mixture of glyceric and tartonic acid is obtained.
- ii. With conc. HNO_3 , mainly glyceric acid is obtained.
- iii. With bismuth nitrate, only mesoxalic acid is obtained.
- iv. Mild oxidising agent, such as Br_2 water, sodium hypobromite (Br_2/NaOH) and Fenton's reagent ($\text{H}_2\text{O}_2 + \text{FeSO}_4$) give a mixture of glyceraldehyde and dihydroxy acetone. This mixture is called glycerose.

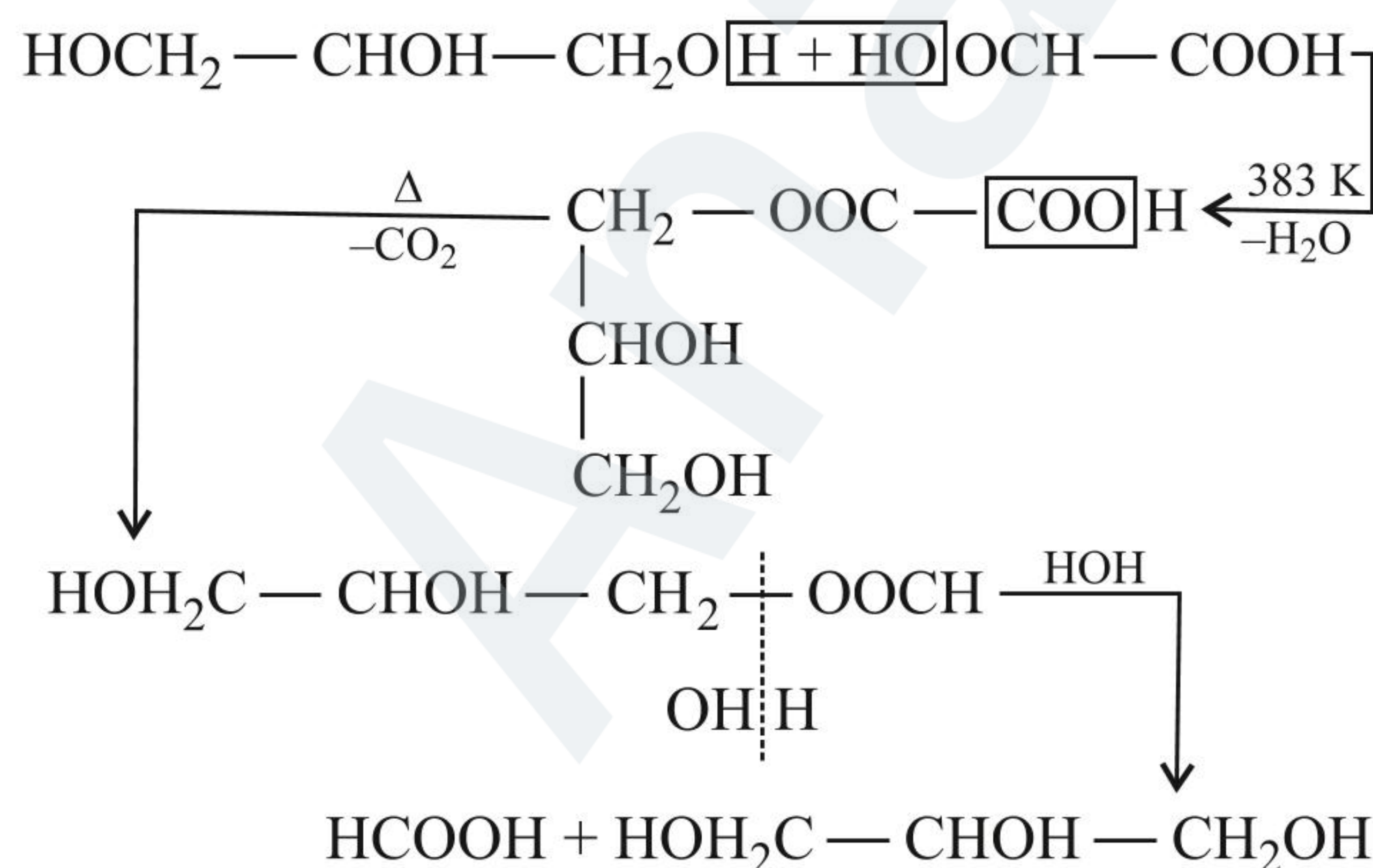
g. Reaction with HIO_4 :



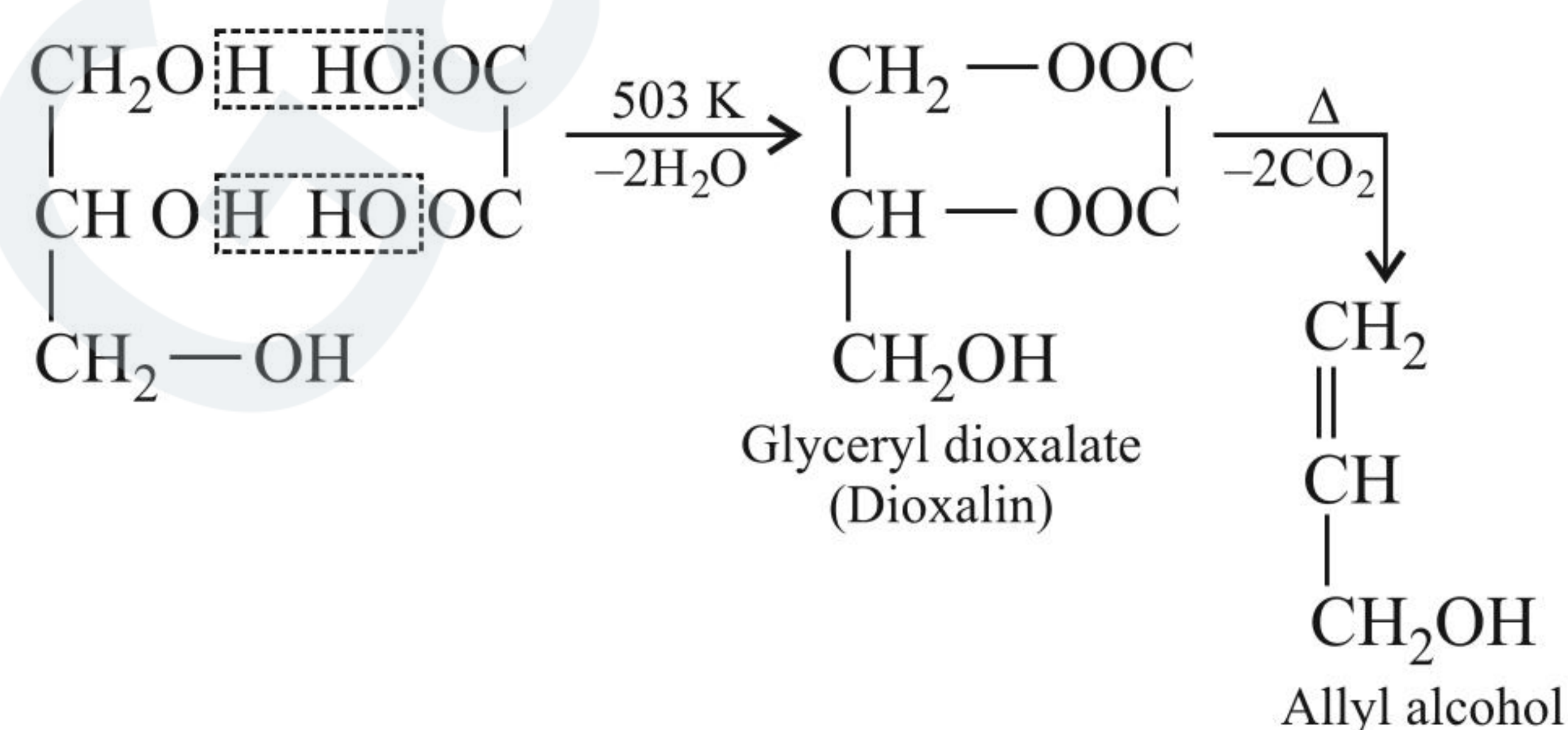
h. With acidic KMnO_4 :



- i. Reaction with oxalic acid:** When oxalic acid is heated with glycerol at 383 K, it forms glycerol mono-oxalate which loses a molecule of CO_2 to give glycerol mono-formate which in turn on hydrolysis gives formic acid.



- ii.** At 230°C (503 K), oxalic acid reacts with glycerol to form glycerol dioxalate which loses two molecules of CO_2 to give allyl alcohol.



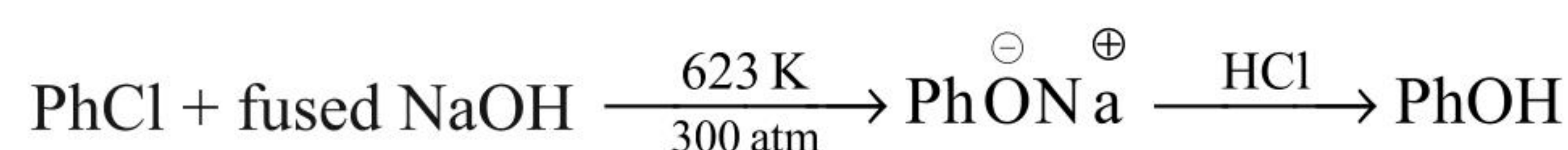
4.10 PREPARATION OF PHENOLS

From middle oil fraction of coal tar distillation

- a.** Phenols (carbolic acid) and cresols are isolated from the middle oil fraction (443–502 K) of the coaltar distillation.

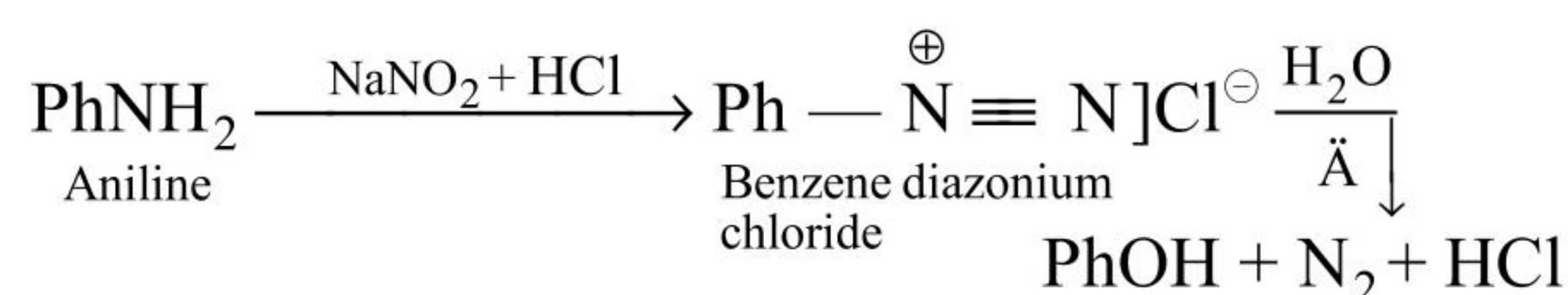
b. From aryl halides (Dow's method)

Phenols are obtained by reacting ArX with fused NaOH at 623 K and 300 atm followed by acidification with HCl .



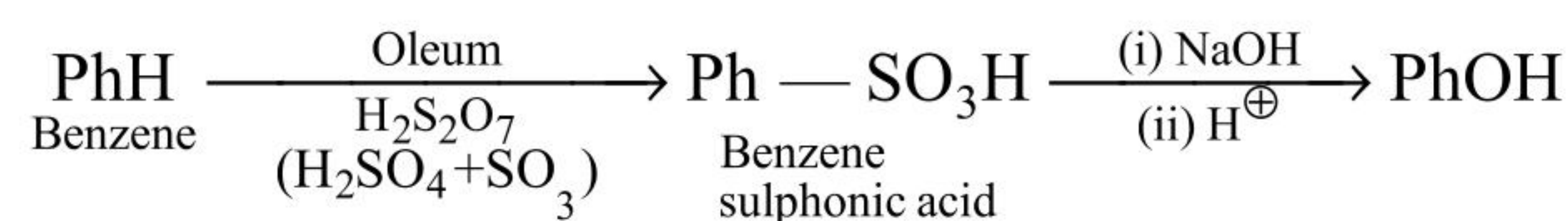
c. From diazonium salts

Aniline on diazotisation with HNO_2 ($\text{NaNO}_2 + \text{HCl}$) at 273–278 K gives benzene diazonium chloride which on hydrolysis by warming with H_2O or by treating with dilute acids gives phenol.



d. From benzene sulfonic acids

Benzene on sulphonation gives benzene sulphonic acid which is converted to sodium phenoxide on heating with molten sodium followed by acidification to give phenol.



e. From cumene

Cumene (isopropyl benzene) is oxidised in the presence of air to cumene hydroperoxide followed by acidification with dilute acid to give phenol and acetone (byproduct).

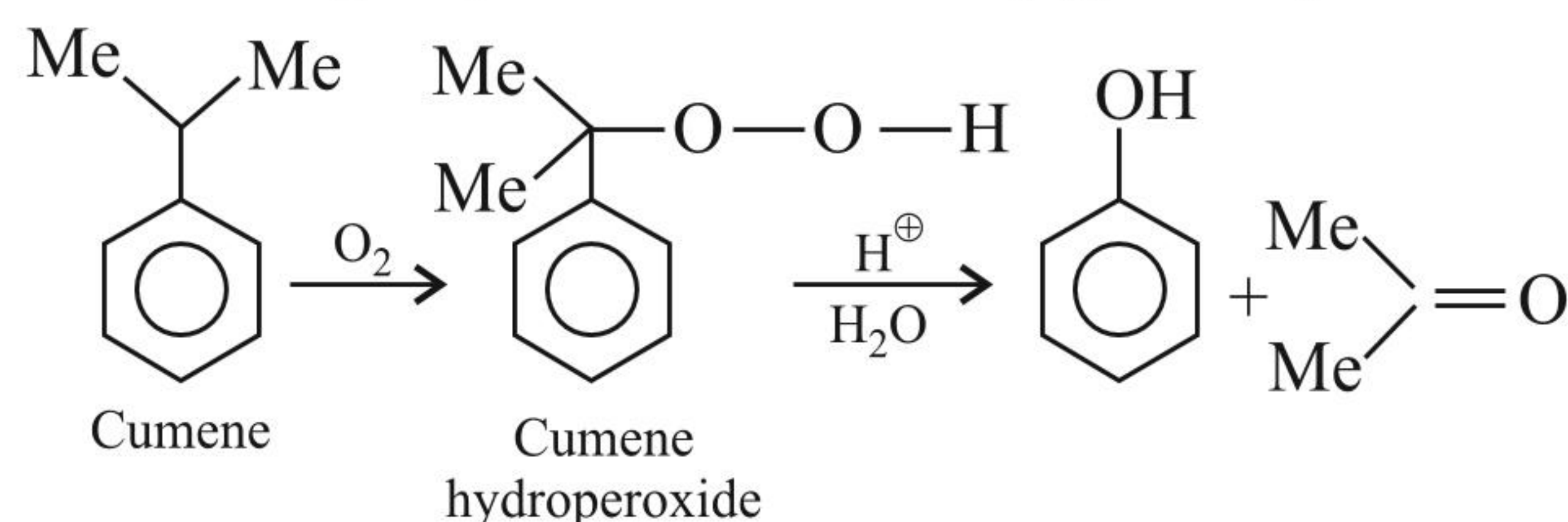


ILLUSTRATION 4.3

Arrange the following compounds in the decreasing order of their boiling points and solubility in H_2O .

- a. (I) Methanol (II) Ethanol
(III) Propan-1-ol (IV) Butan-1-ol
(V) Butan-2-ol (VI) Pentan-1-ol
- b. (I) Pentanol (II) *n*-Butane
(III) Pentanal (IV) Ethoxy ethane
- c. (I) Pentane (II) Pentane-1,2,3-triol
(III) Butanol
- d. (I) Butane (II) Butanol
(III) Pentanol

Sol.

- a. **Boiling point order:** VI > IV > V > III > II > I

Solubility order: I > II > III > V > IV > VI

Explanation: All of them are alcohols, so all have H-bonding. As the molecular mass and surface area increases, the boiling point increases and solubility decreases.

Out of (IV) and (V), there is branching in (V) and has less surface area than (IV), so the boiling point of (IV) > (V), but solubility of (V) > (IV).

- b. **Boiling point order:** I > III > IV > II

Solubility order: I > III > IV > II

In (I), there is H-bonding, in (II) (aldehyde), dipole-dipole interaction, in (III) (ether), slightly polar due to EN of O, and in (IV) (alkane), van der Waals interaction (non-polar).

- c. **Boiling point order:** II > III > I

Solubility order: II > III > I

In (II), three (—OH) groups, more H-bonding; in (III), one (—OH) group, less H-bonding; in (I) (alkane), van der Waals interaction.

- d. **Boiling point order:** III > II > I

Solubility order: II > III > I

Both (II) and (III) have H-bonding, but molecular mass of (III) > (II), hence the given boiling point order.

Solubility of (II) > (III), because in (III), size of R-group non-polar (hydrophobic part) is larger, hence the given solubility order.

ILLUSTRATION 4.4

Explain the following:

- a. Which has higher boiling point?
(I) Phenol (II) Benzenethiol
- b. Which has higher melting point?
(I) Hydroquinone (II) Catechol
- c. Explain the less solubility and lower boiling point of:
(I) *o*-Nitrophenol
(II) *o*-Hydroxy benzaldehyde
(III) *o*-Hydroxybenzoic acid (salicylic acid) compared with their *p*- and *m*-isomers.
- d. Which isomer (*o*, *m*-, or *p*) of hydroxy acetophenone is steam volatile?
- e. Which of the following shows chelation?
(I) *o*-Cresol (II) Oil of wintergreen
(III) *o*-Iodo phenol (IV) *o*-Fluoro phenol
(V) *o*-Cyano phenol
- f. Compare the boiling points and water solubilities of phenol and toluene.
- g. Why are monophenolic compounds (e.g., cresols) are insoluble in H_2O ?
- h. Which is more soluble in H_2O : hexanol (I) or cyclohexanol (II)?

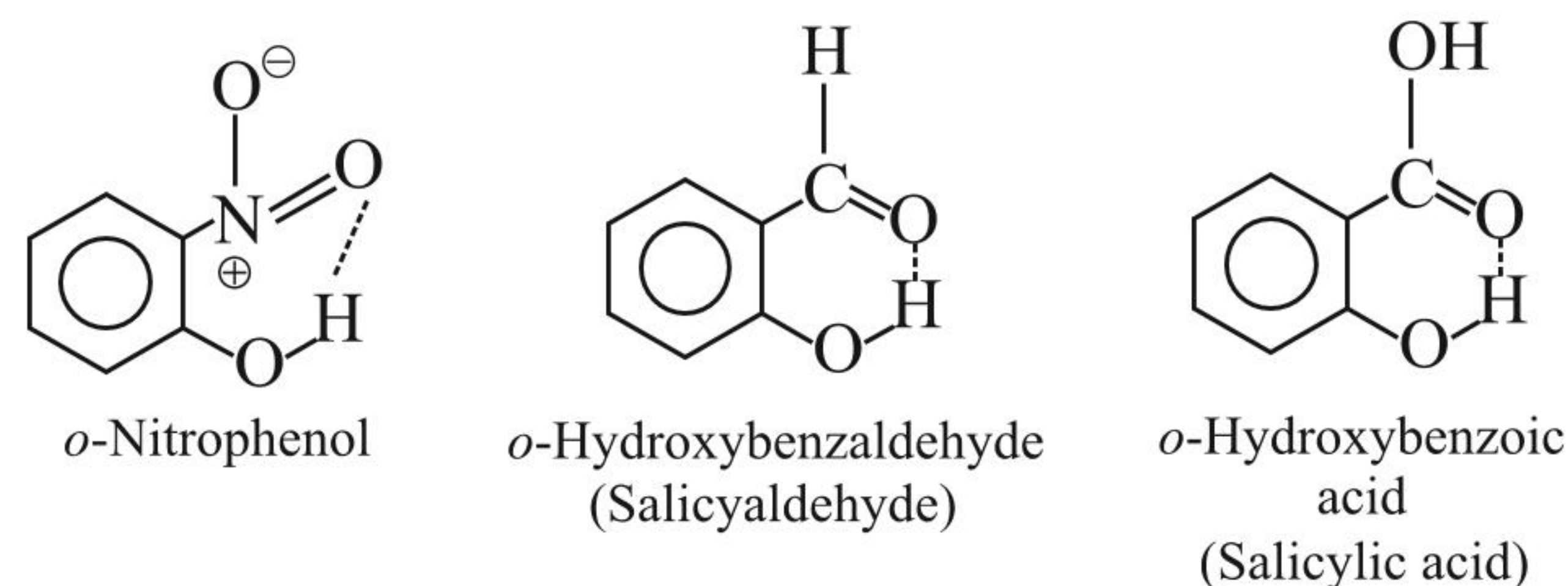
Sol.

- a. Although the molecular mass of benzenethiol (Ph—SH) is higher, phenol has high boiling point. It is because there is no H-bonding in PhSH .

- b. Hydroquinone ($\text{HO—C}_6\text{H}_4\text{—OH}$) (I) has high melting point than catechol ($\text{C}_6\text{H}_4(\text{OH})_2$) (II), because of the

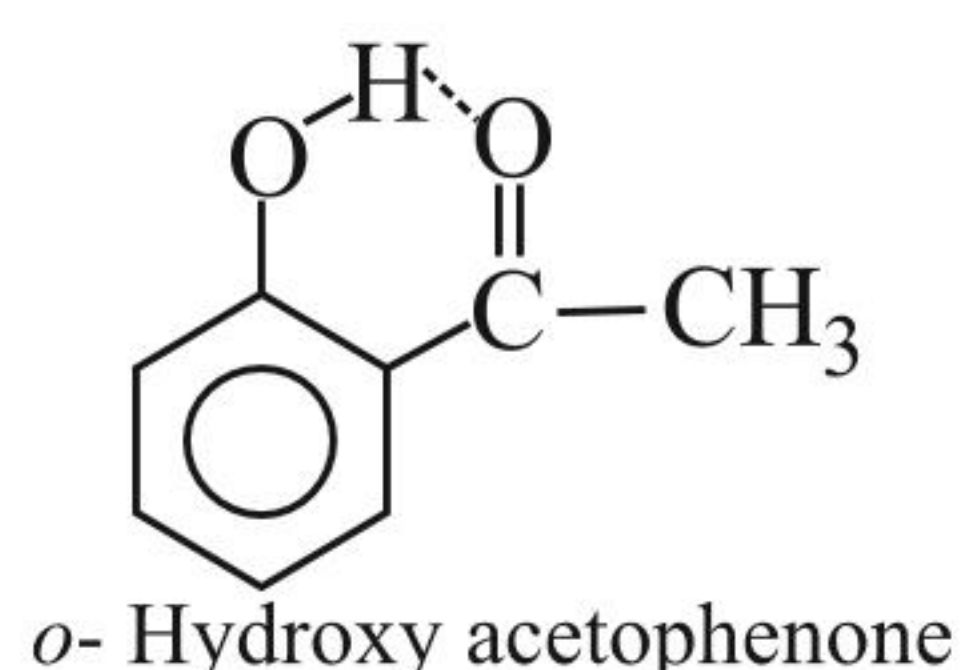
symmetrical packing of *p*-isomer (I) in its crystal lattice which requires more energy for its melting.

- c. In *ortho*-isomers of (I), (II), and III, intramolecular H-bonding (chelation) occurs which inhibits the intermolecular attraction between these molecules and thus lowers the boiling point and also reduces H-bonding of these molecules with H_2O , thereby, decreases water solubility. Intramolecular chelation does not occur in *p*- and *m*-isomers.

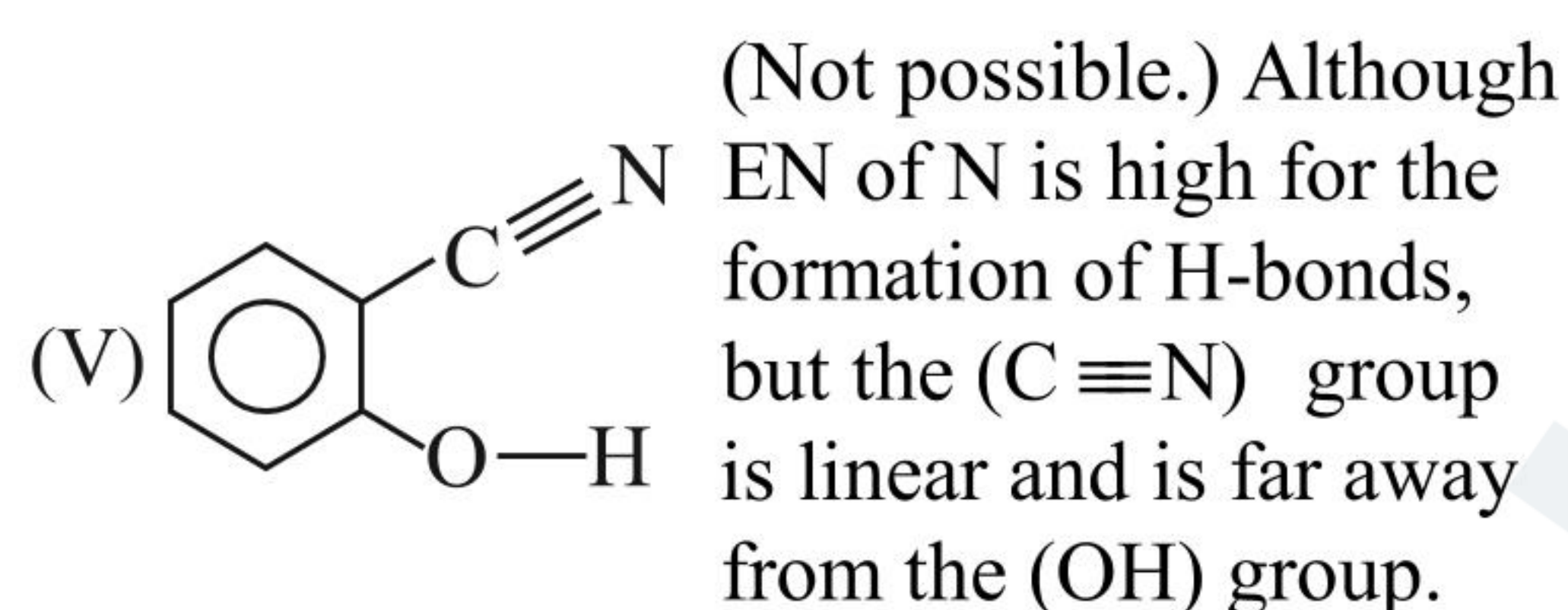
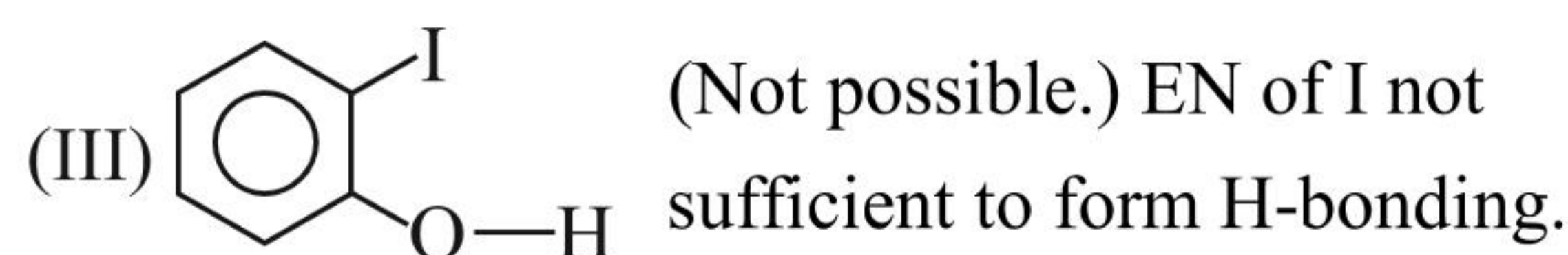
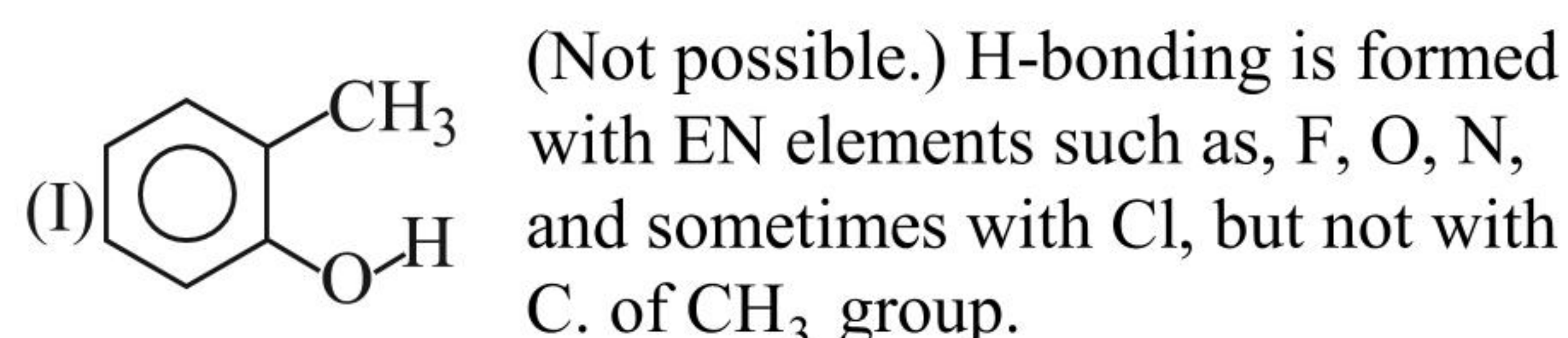
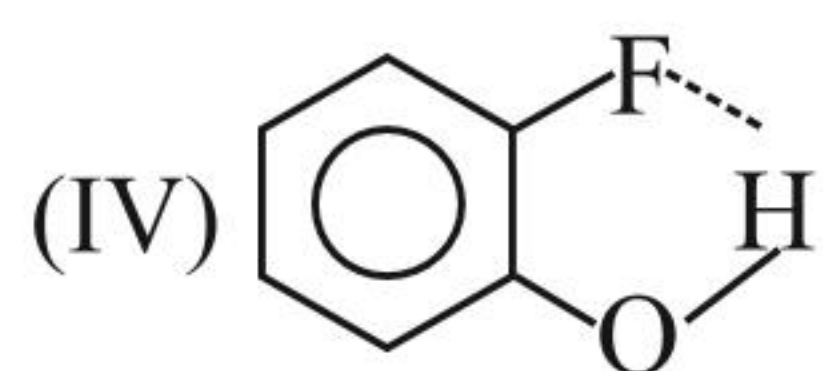
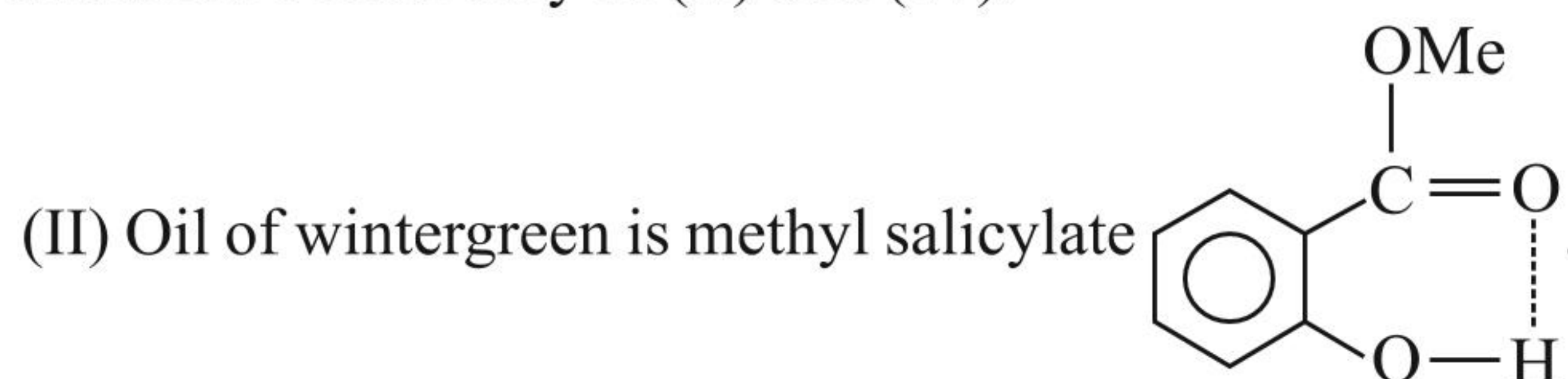


- d. Chelated *o*-isomers have a minimum attraction with H_2O , and they are steam volatile or steam distills. Steam volatile

or steam distills are the compounds which are mixed with boiling H_2O but not dissolved. On passing steam to such boiling mixture, steam carries the compound with it.



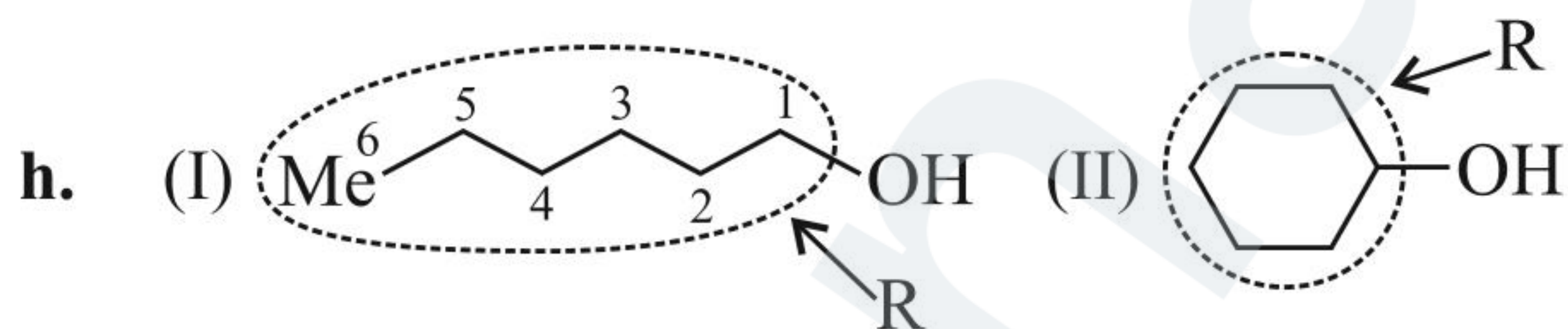
e. Chelation occurs only in (II) and (IV).



Therefore, H-bonding cannot occur.

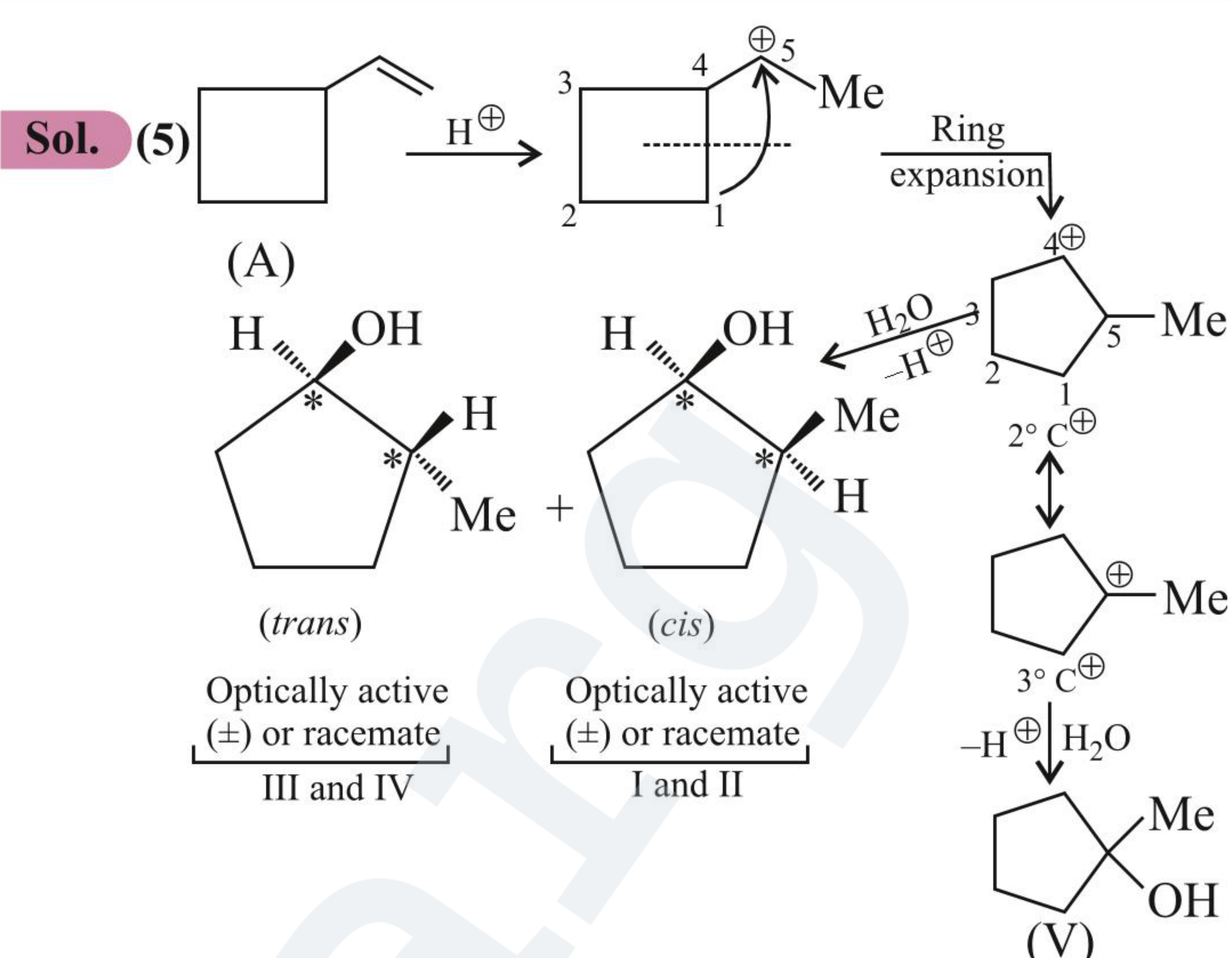
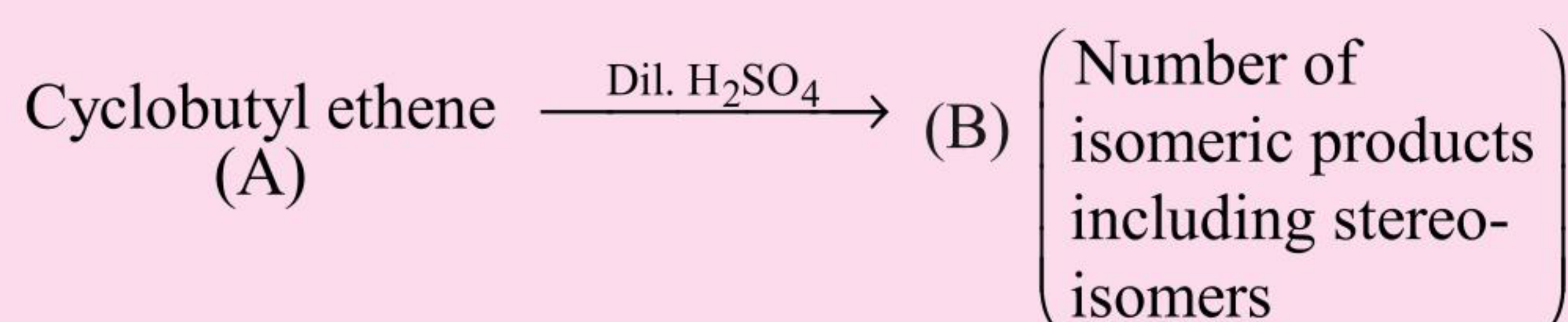
f. Boiling point as well as water solubility of phenol (181.6°C) is greater than that of toluene (110.5°C) because of intermolecular H-bonding.

g. The increase in molecular mass and large non-polar part (hydrophobic) dominate over the solubilising effect of H-bonding.



The alkyl group (R) in (II) is more compact than in (I) and hence (OH) group is more exposed and available for H-bonding with H_2O . In other words, (II) has less surface area than (I), and hence more solubility.

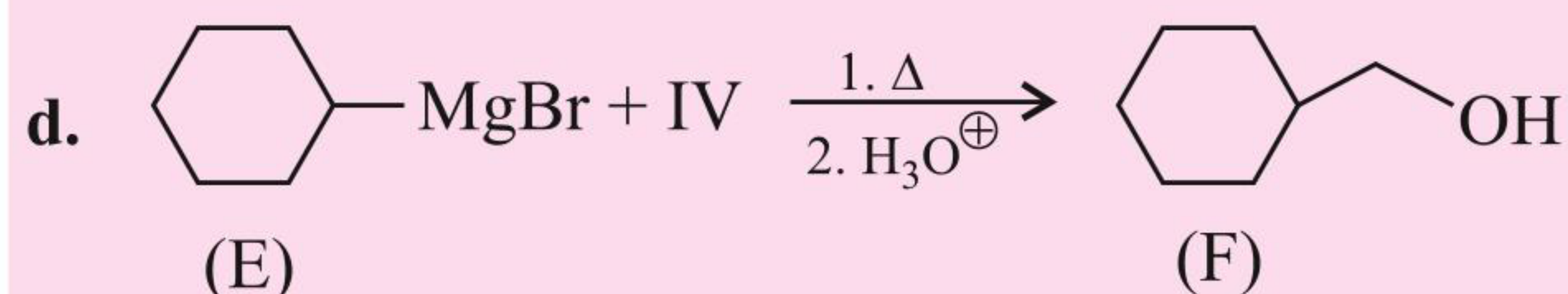
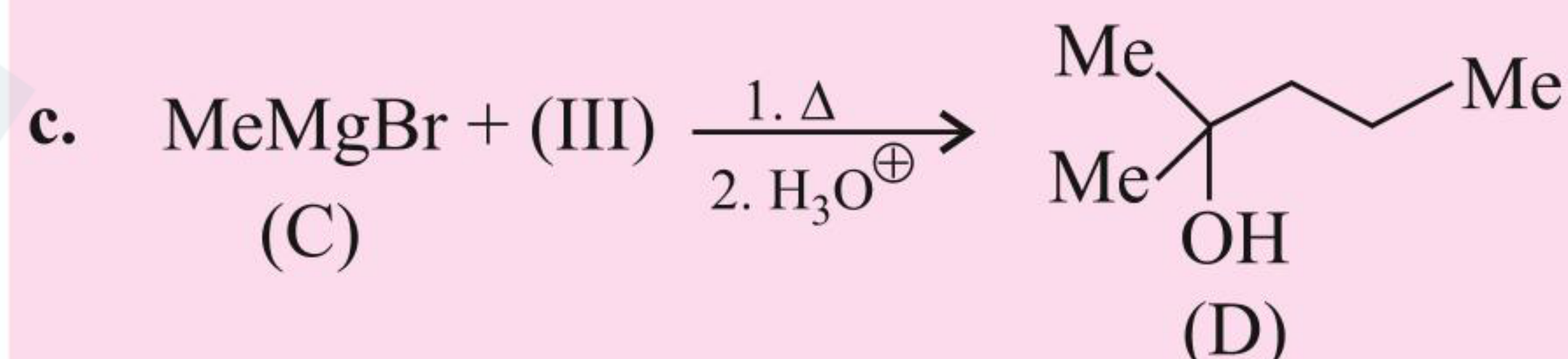
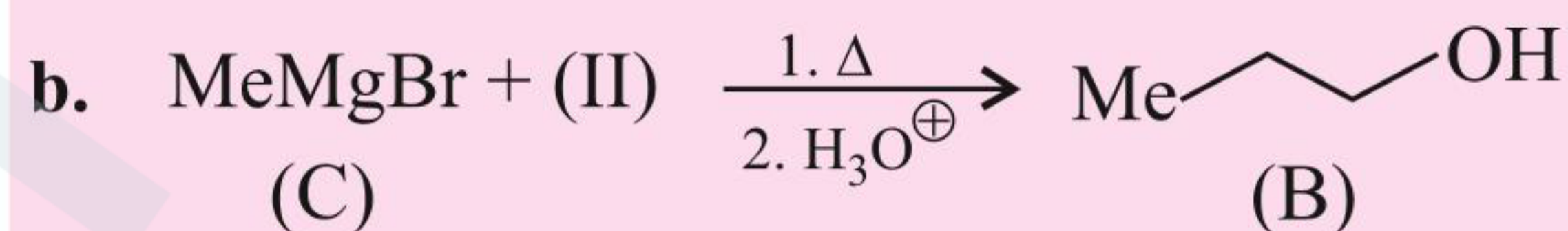
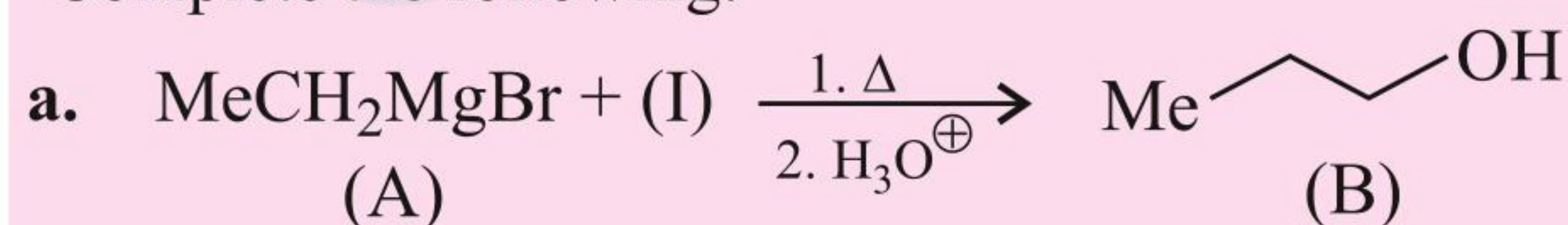
ILLUSTRATION 4.5



The total number of isomeric products including stereo-isomers is 5.

ILLUSTRATION 4.6

Complete the following:



Sol.

a. (B) is 1° alcohol, with 3C, and G.R. contains 2C \rightarrow , so (I) is $(\text{CH}_2 = \text{O})$ (methanal).

b. (B) is 1° alcohol with 3C, and G.R. contains 1C, so (II) is $\left(\triangle \text{O} \right)$ (ethylene oxide).

c. (D) is 3° alcohol with 6C, and G.R. contains 1C, so (III) is ketone with 5C.

So (III) is $\left(\text{Me}-\underset{5}{\text{CH}_2}-\underset{4}{\text{CH}_2}-\underset{3}{\text{CH}_2}-\underset{2}{\text{CO}}-\underset{1}{\text{Me}} \right)$ (pentan-2-one)
or $\text{MeCH}_2\text{CH}_2\text{COMe}$.

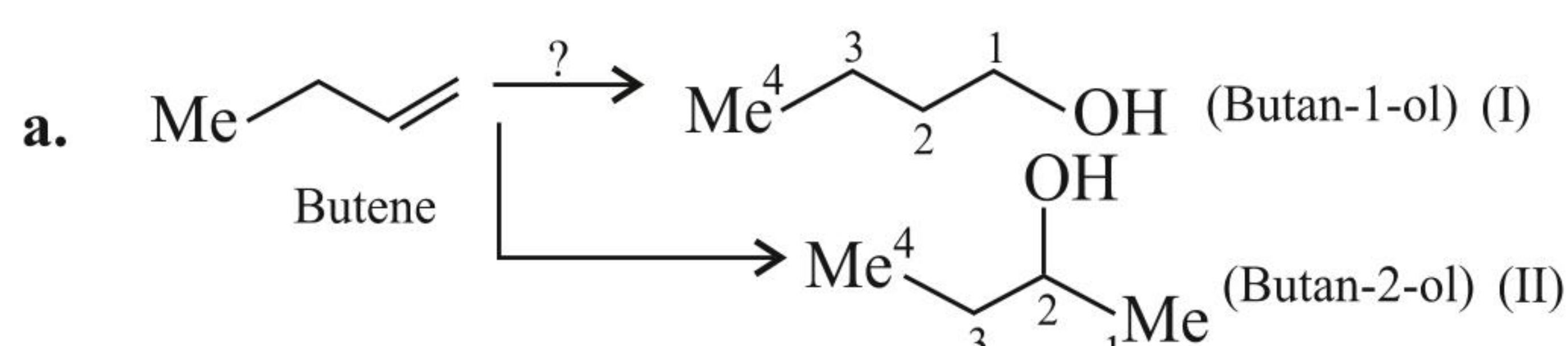
d. (F) is 1° alcohol with 1C more than G.R. (E), so (IV) is $(\text{CH}_2 = \text{O})$ (methanal).

ILLUSTRATION 4.7

Synthesise the following:

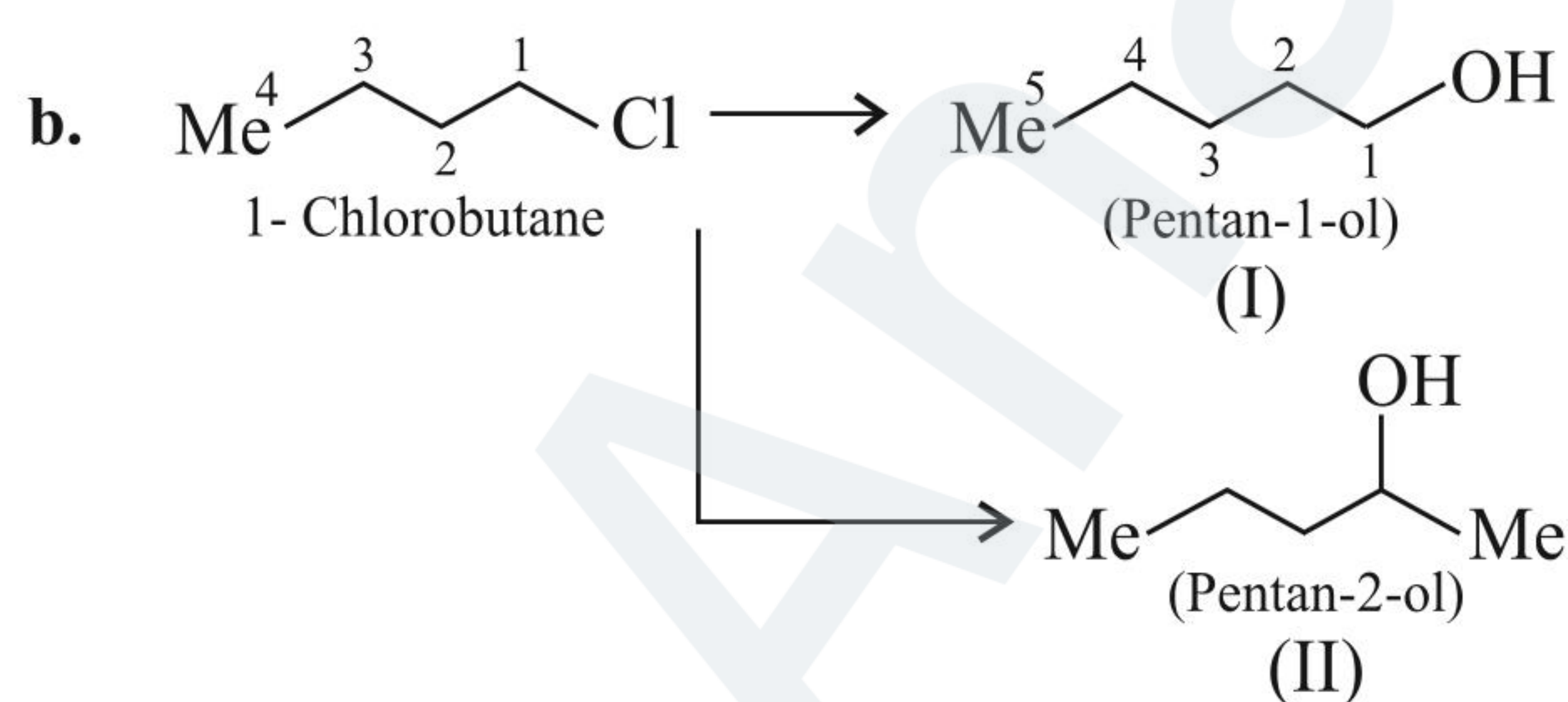
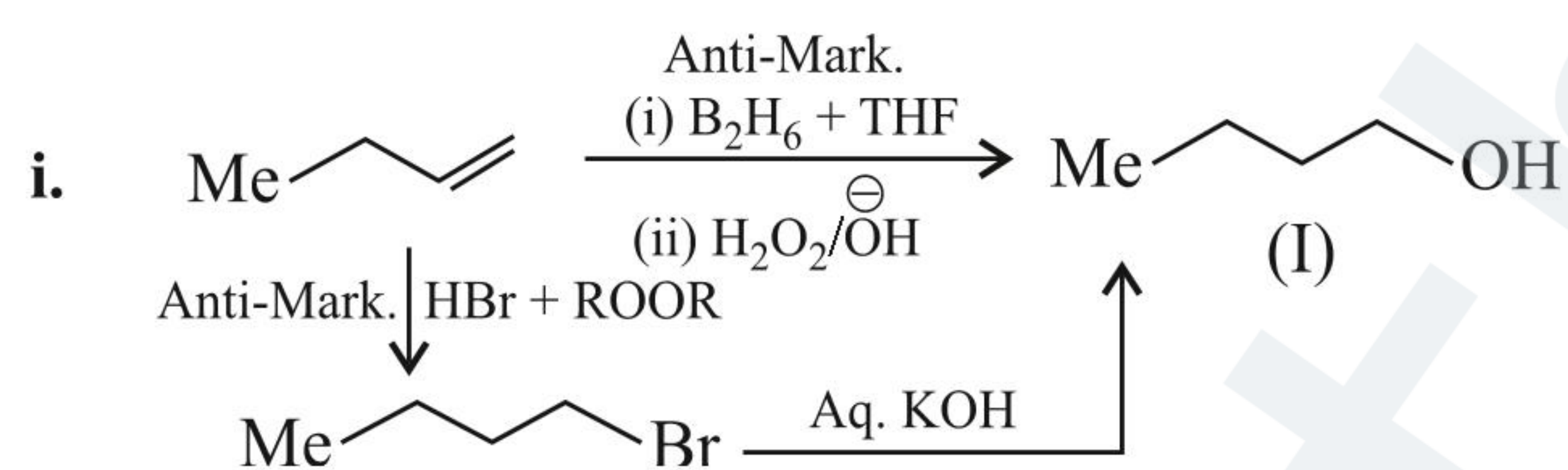
- Butene to butanol (I) and butan-2-ol (II)
- 1-Chlorobutane to pentanol (I) and pentan-2-ol
- 1-Chloropropane to pentanol and pentan-2-ol
- Benzene to 3-(4-chlorophenyl)propan-1-ol
- Ethyne to butanol
- Propane to allyl alcohol
- Propane to propanol and propan-2-ol

Sol.

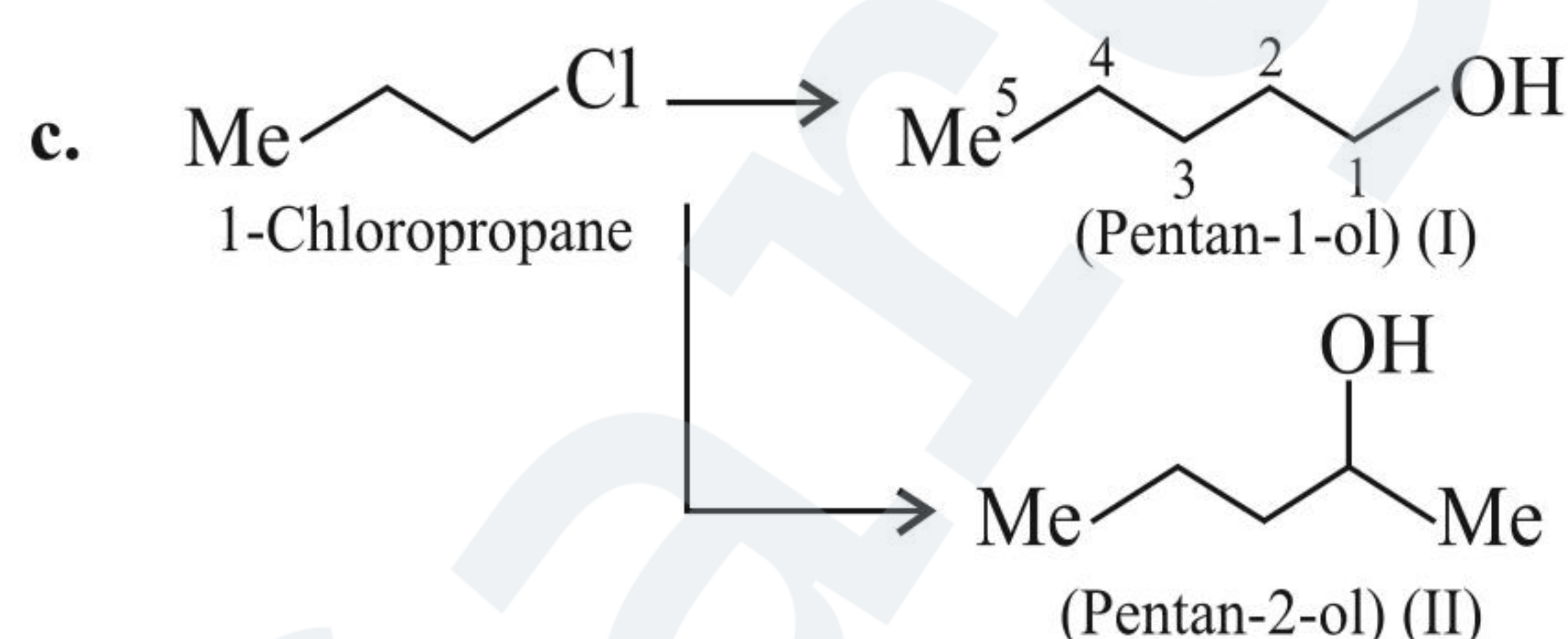
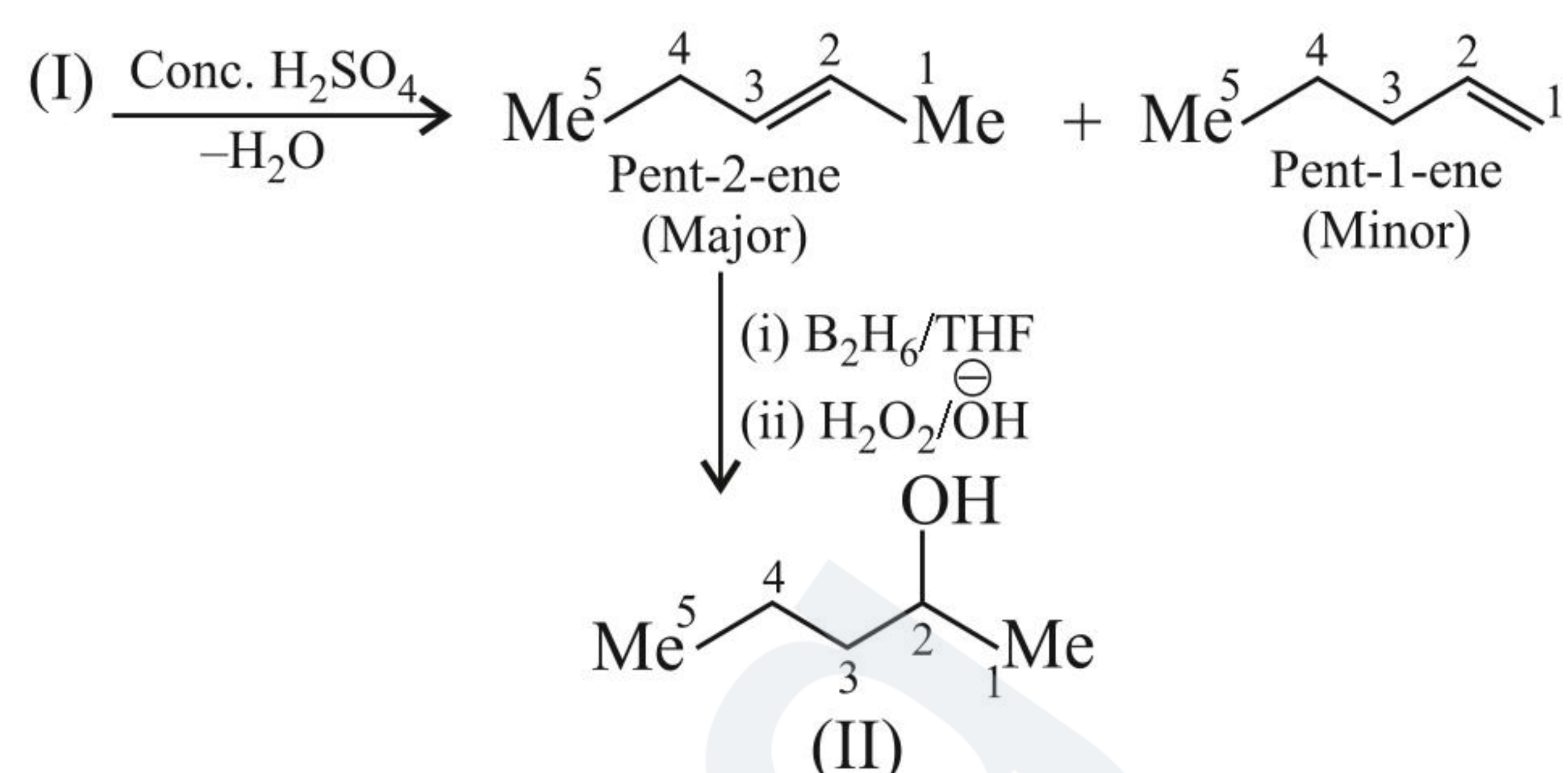
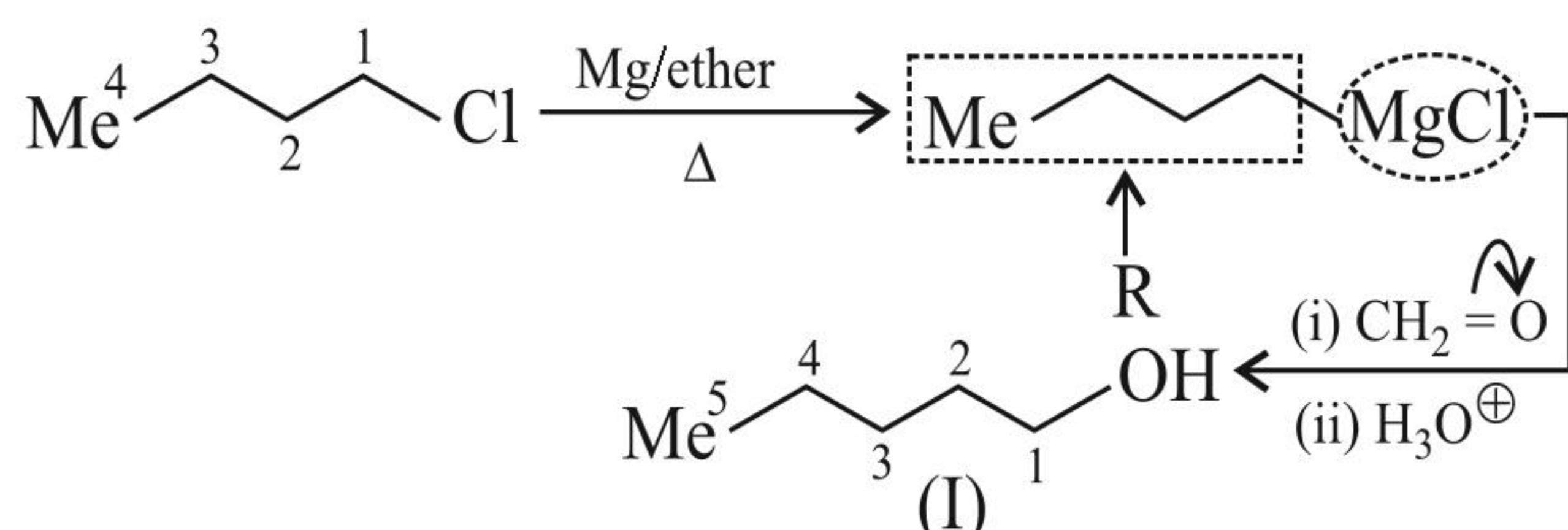


Hydroboration oxidation proceeds with anti-Markovnikov addition, so it would give (I), while acid-catalysed hydration and mercuric-demercuration reaction proceed with Markovnikov addition, so it would give (II).

Synthesis:

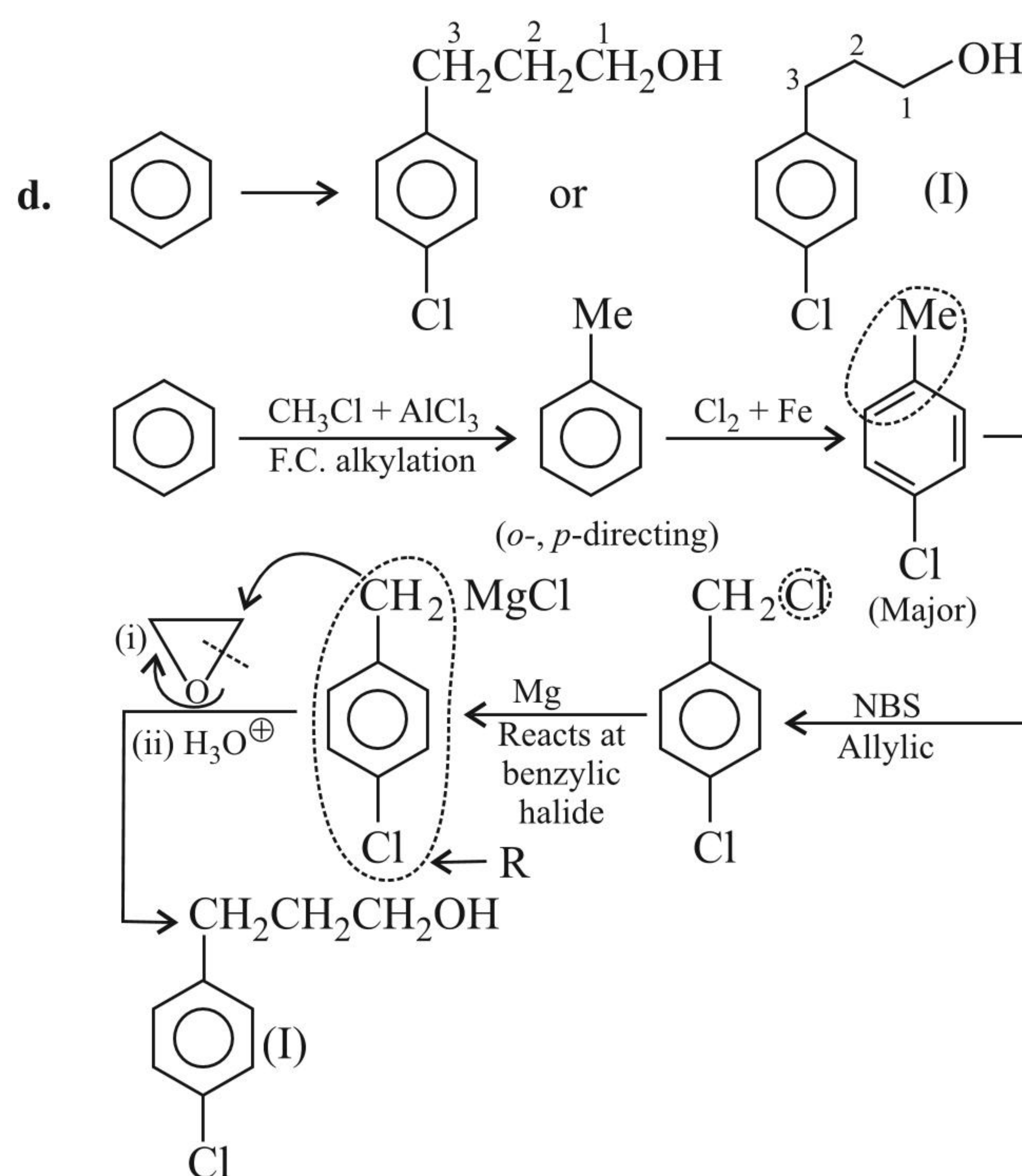
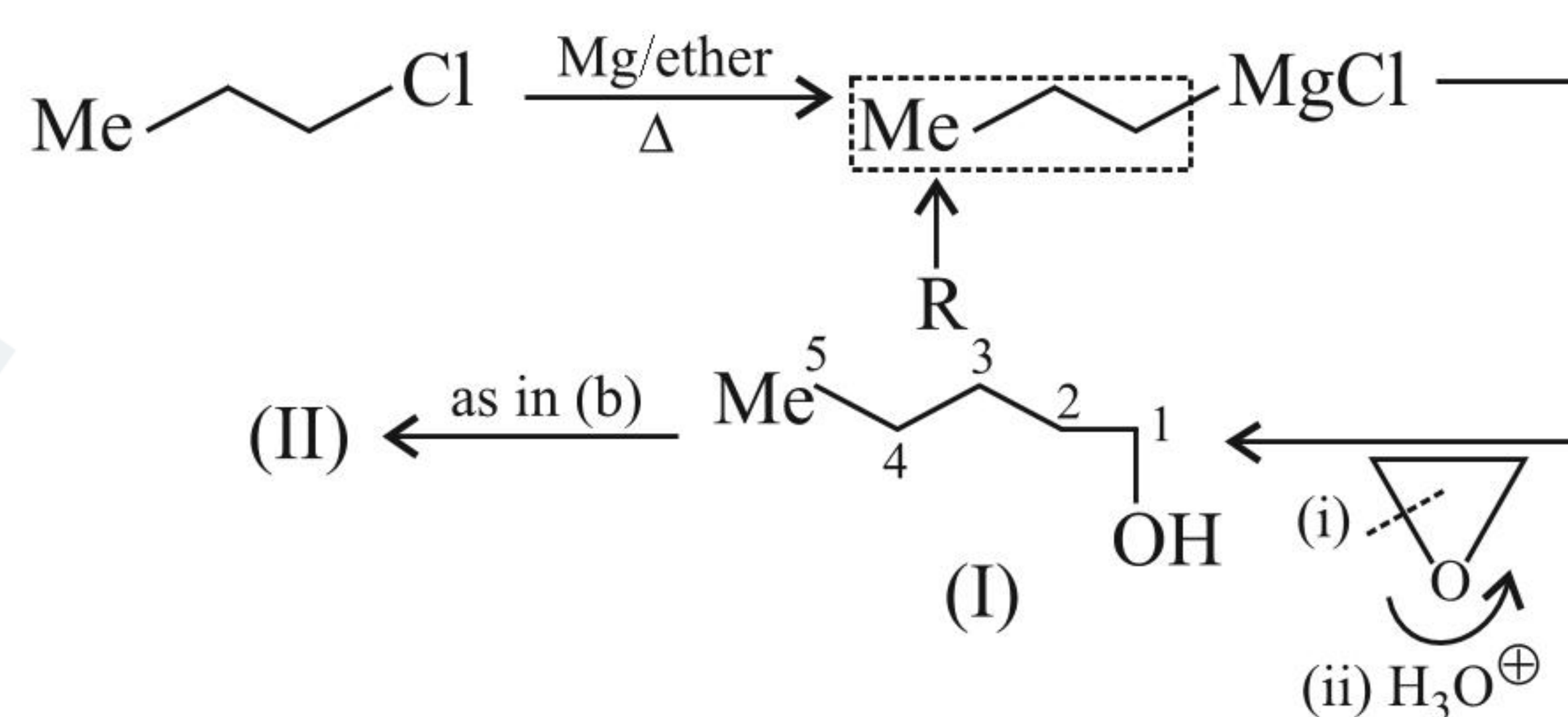


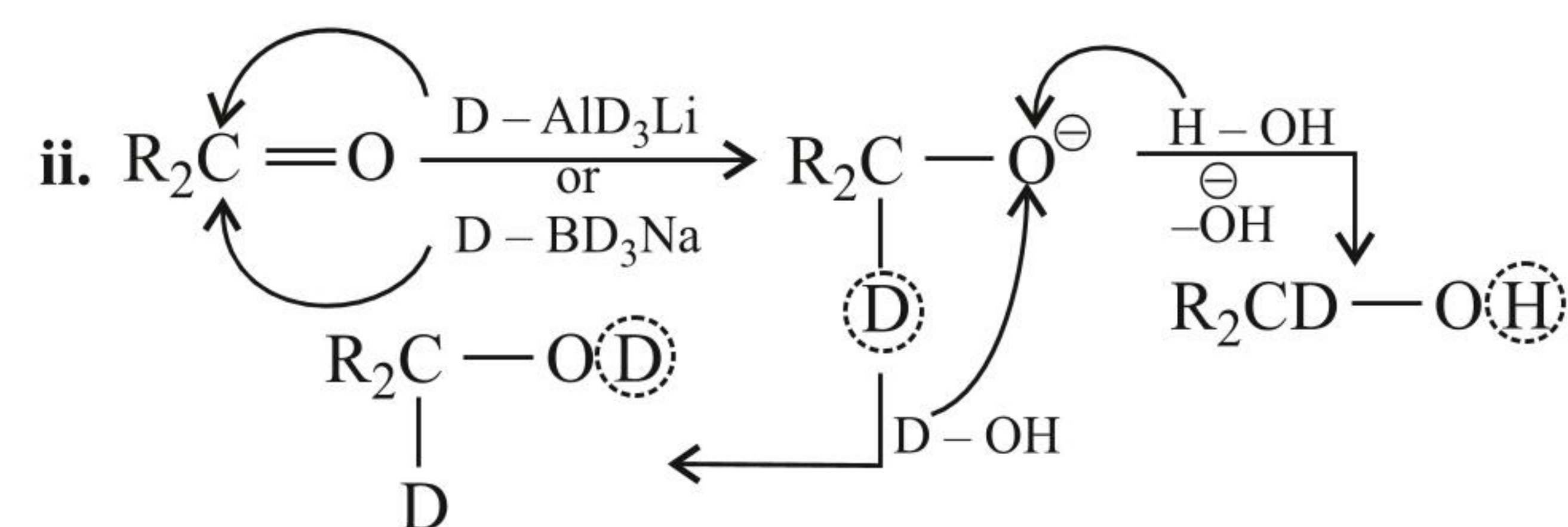
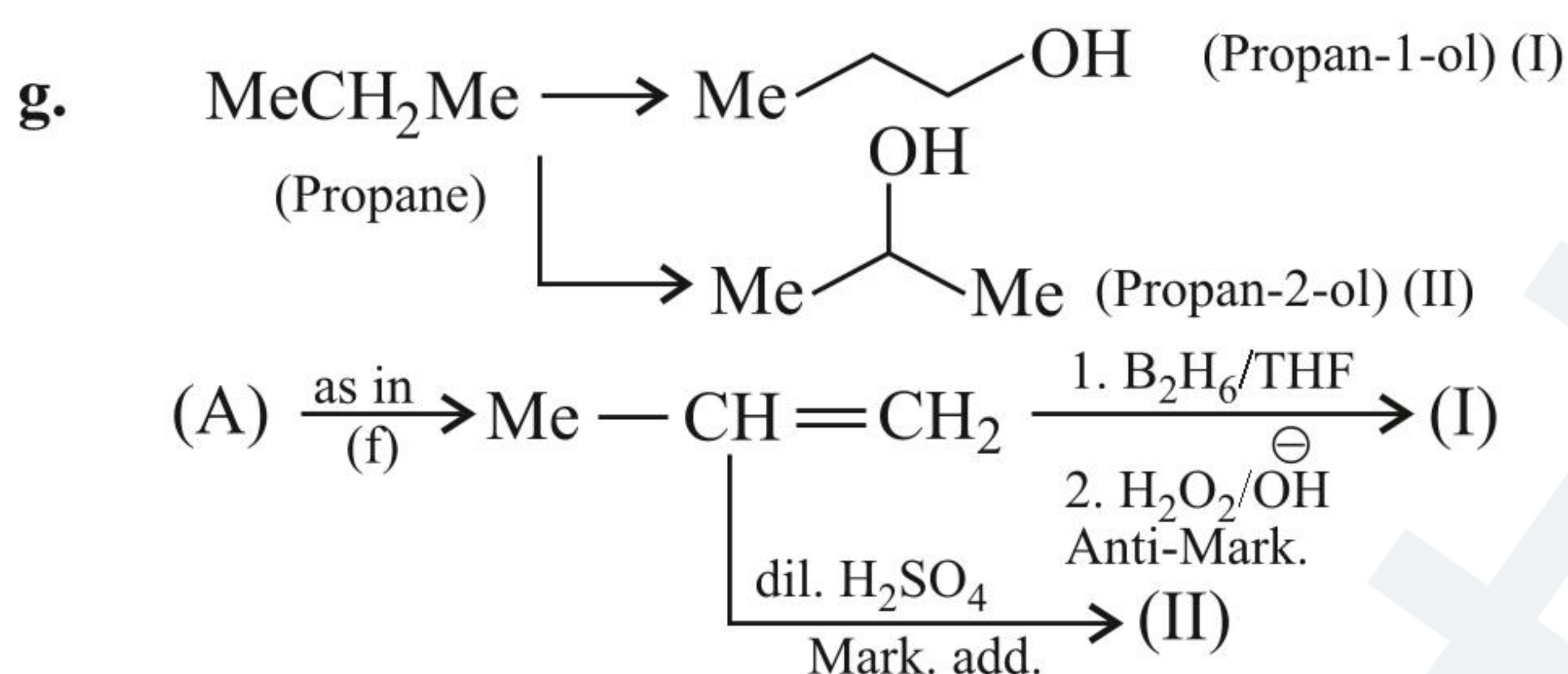
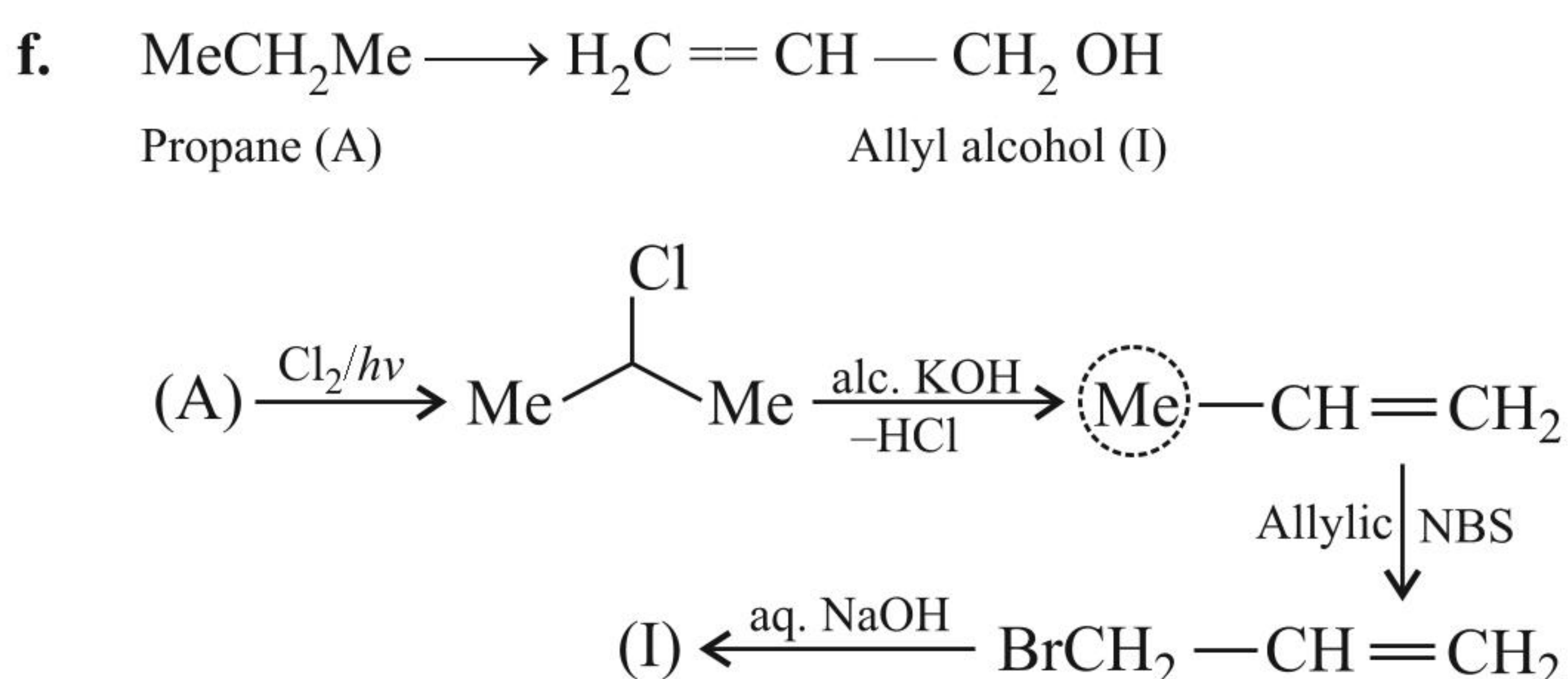
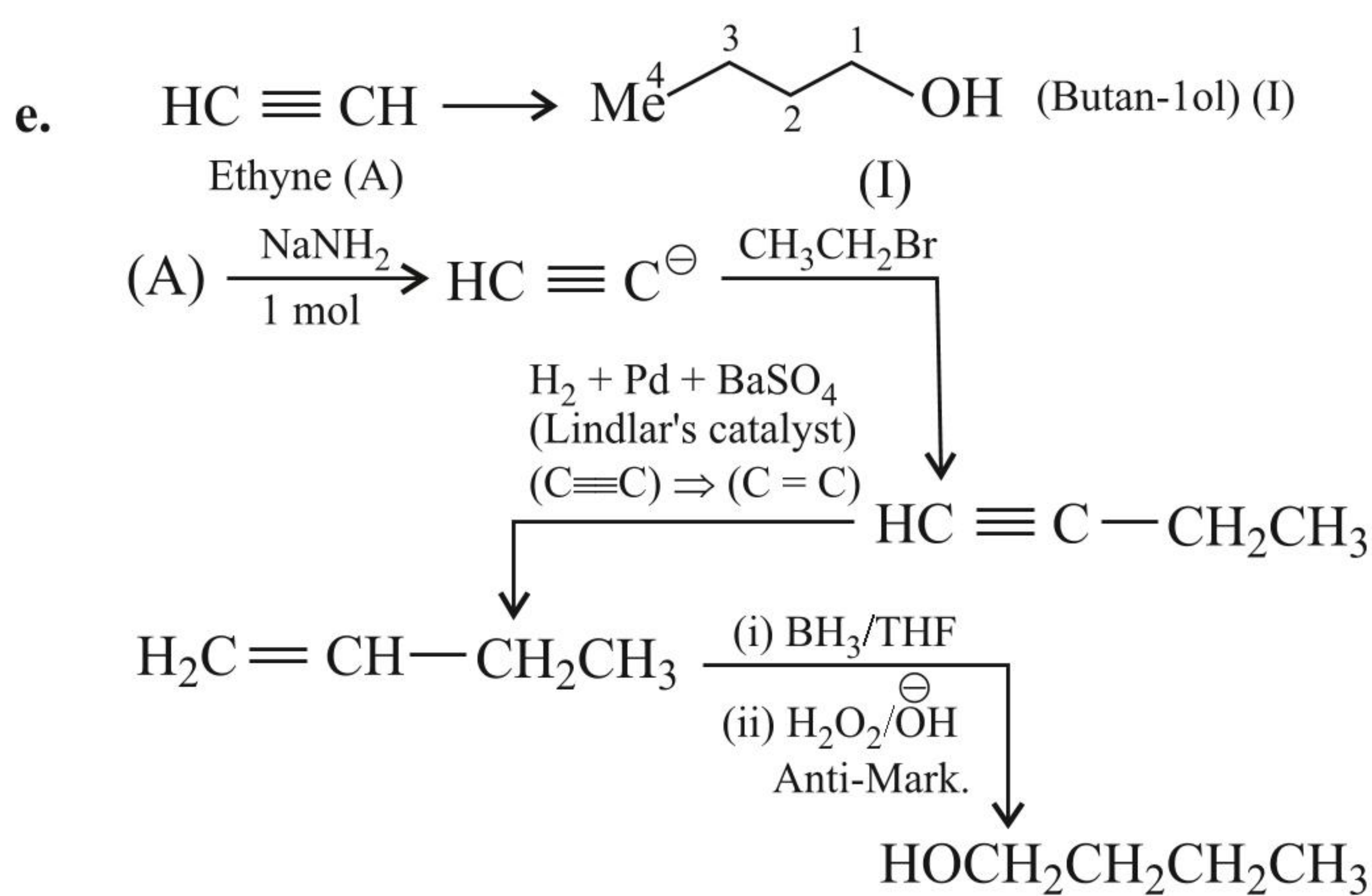
The 4C-atom chain has to be increased to 5C-chain by a G.R. with $\text{CH}_2=\text{O}$.



The 3C-atom chain has to be increased to 5C-chain by a

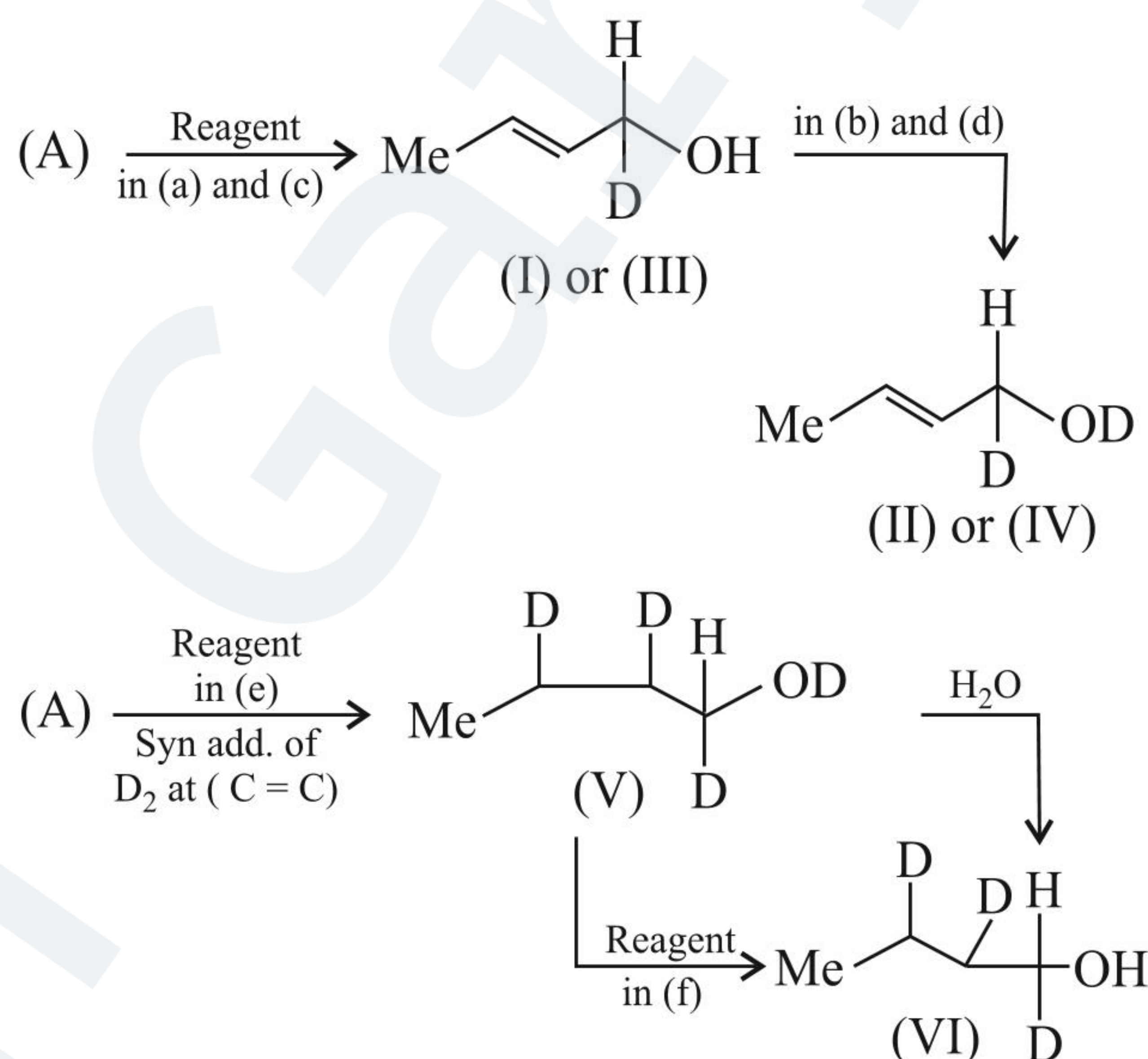
G.R. with ethylene oxide





iii. LAH and NaBH_4 do not reduce $(\text{C} = \text{C})$ bond, whereas catalytic hydrogenation reduces $(\text{C} = \text{C})$ bond to $(\text{C} \text{---} \text{C})$ bond.

iv. LAH and catalytic hydrogenation reduce epoxide but NaBH_4 does not.



The D of ROD rapidly exchanges for the H of H_2O .

Mechanism in (B):

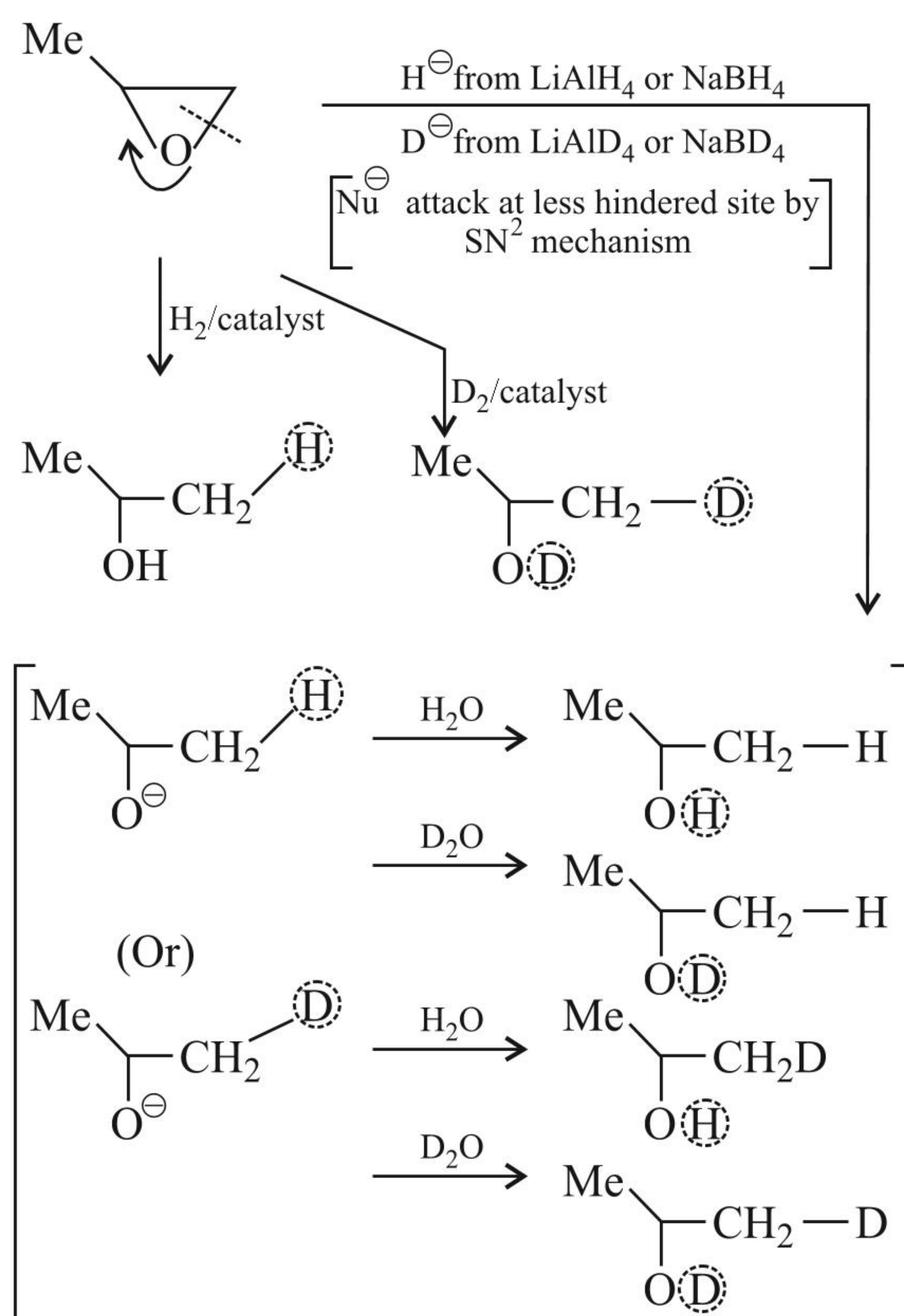
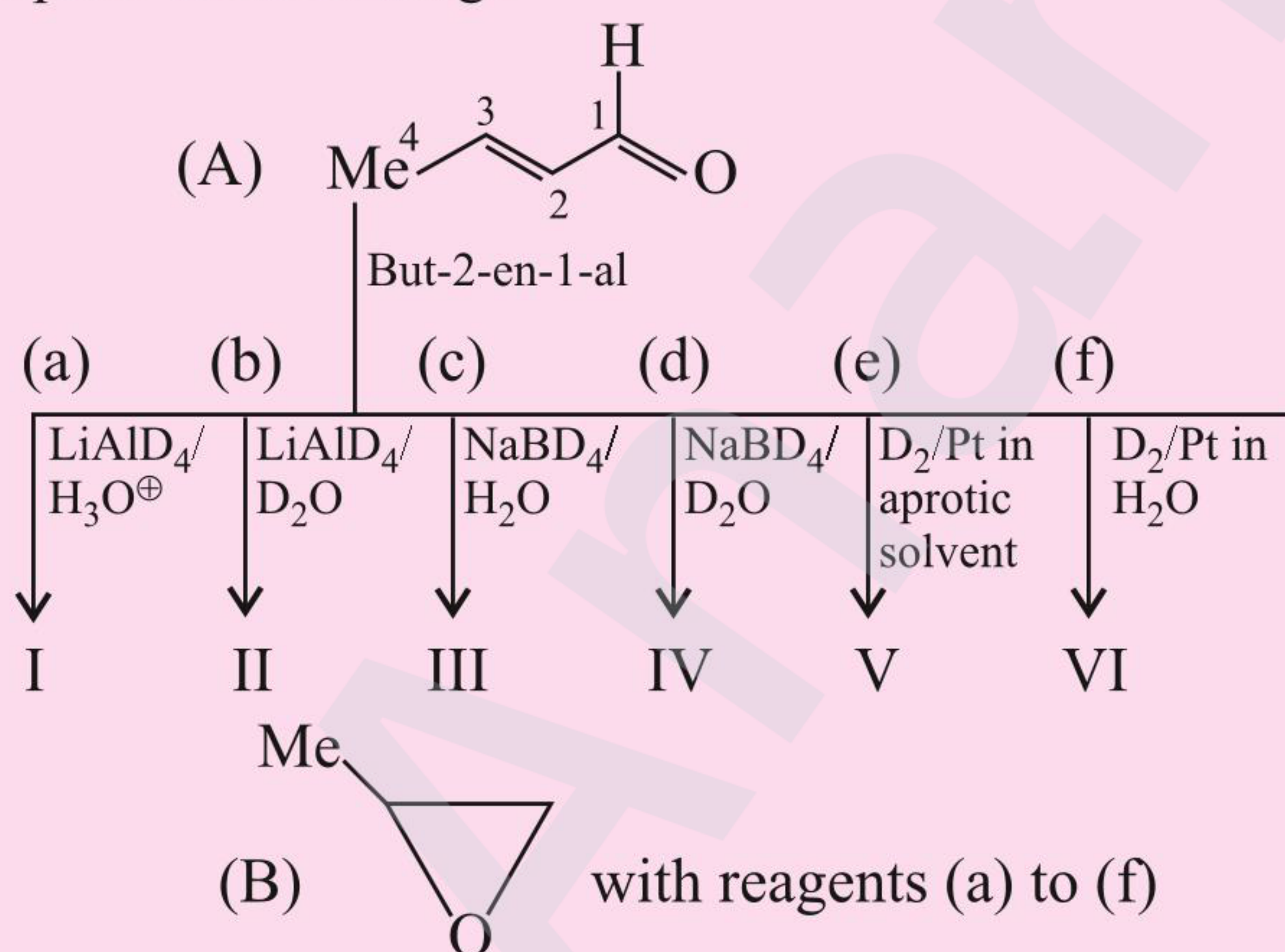


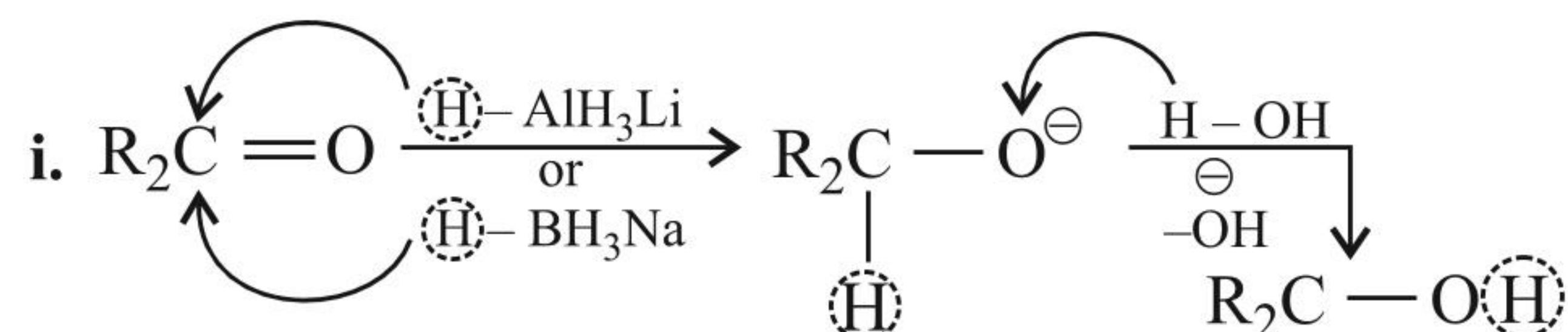
ILLUSTRATION 4.8

Complete the following:

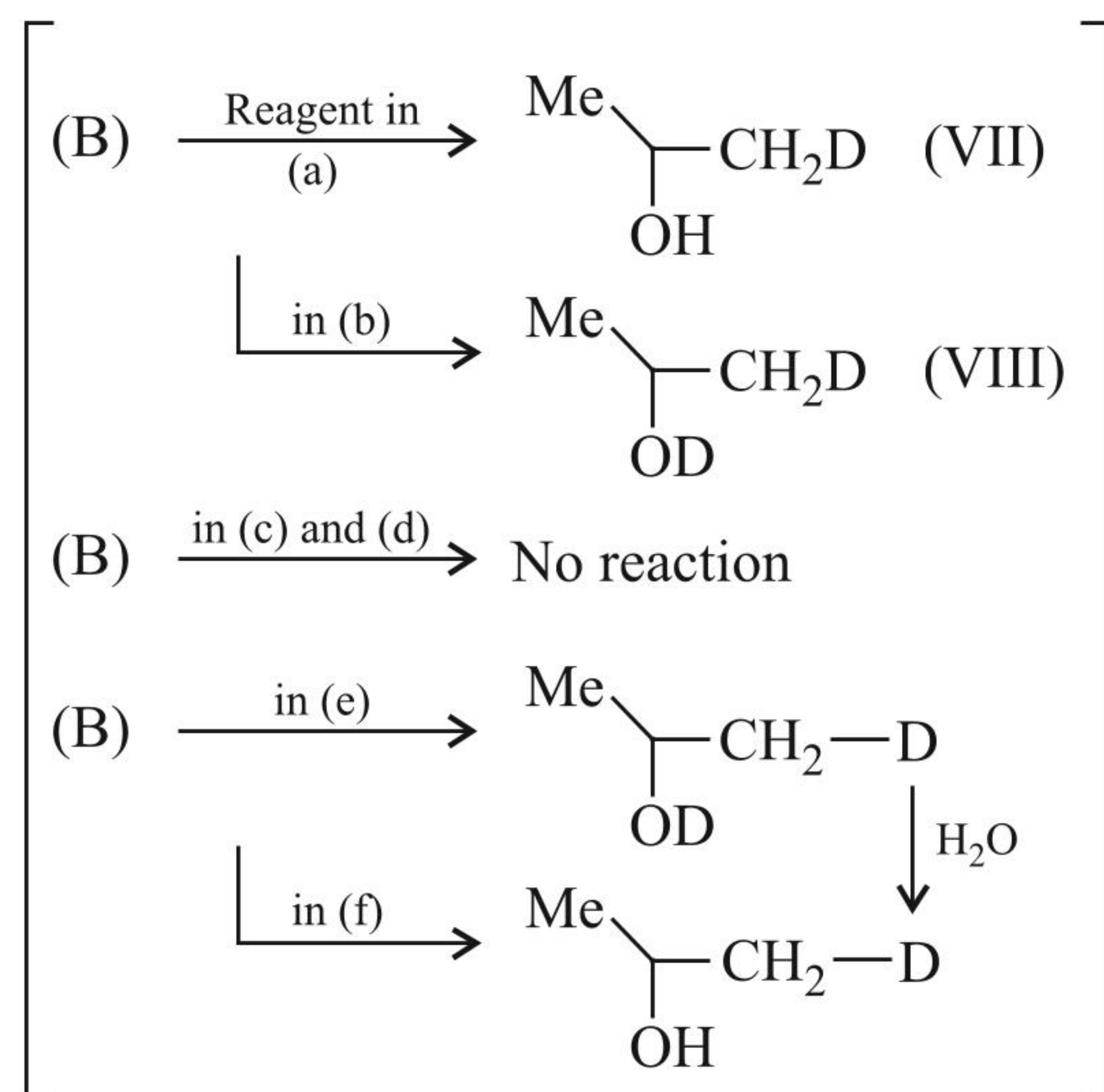


Sol. Mechanism in (A):

[D from LiAlD_4 and NaBD_4 is added to C of $(\text{C} = \text{O})$ group and solvent gives H or D to O atom to form OH or OD, e.g.,]



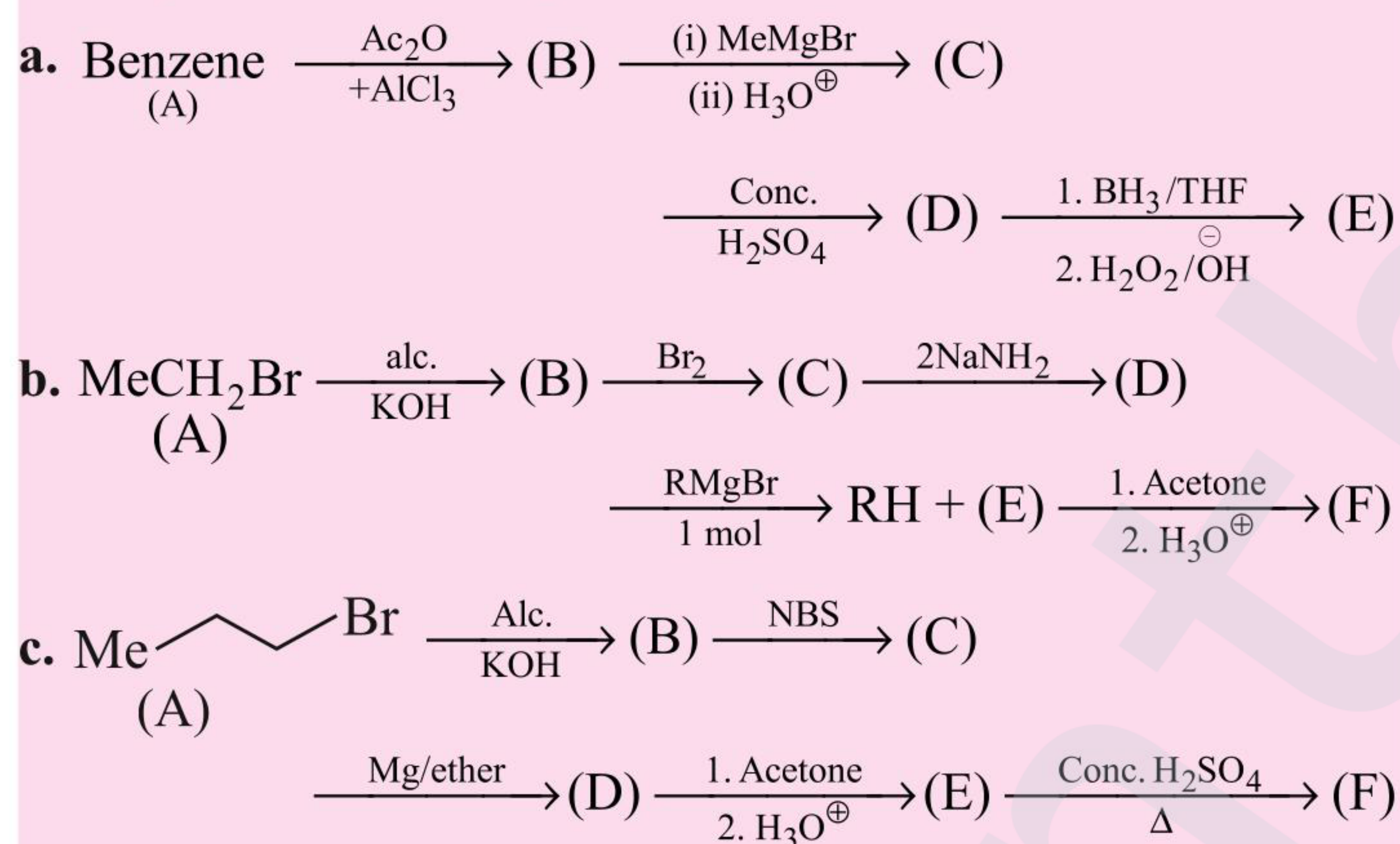
Reactions:



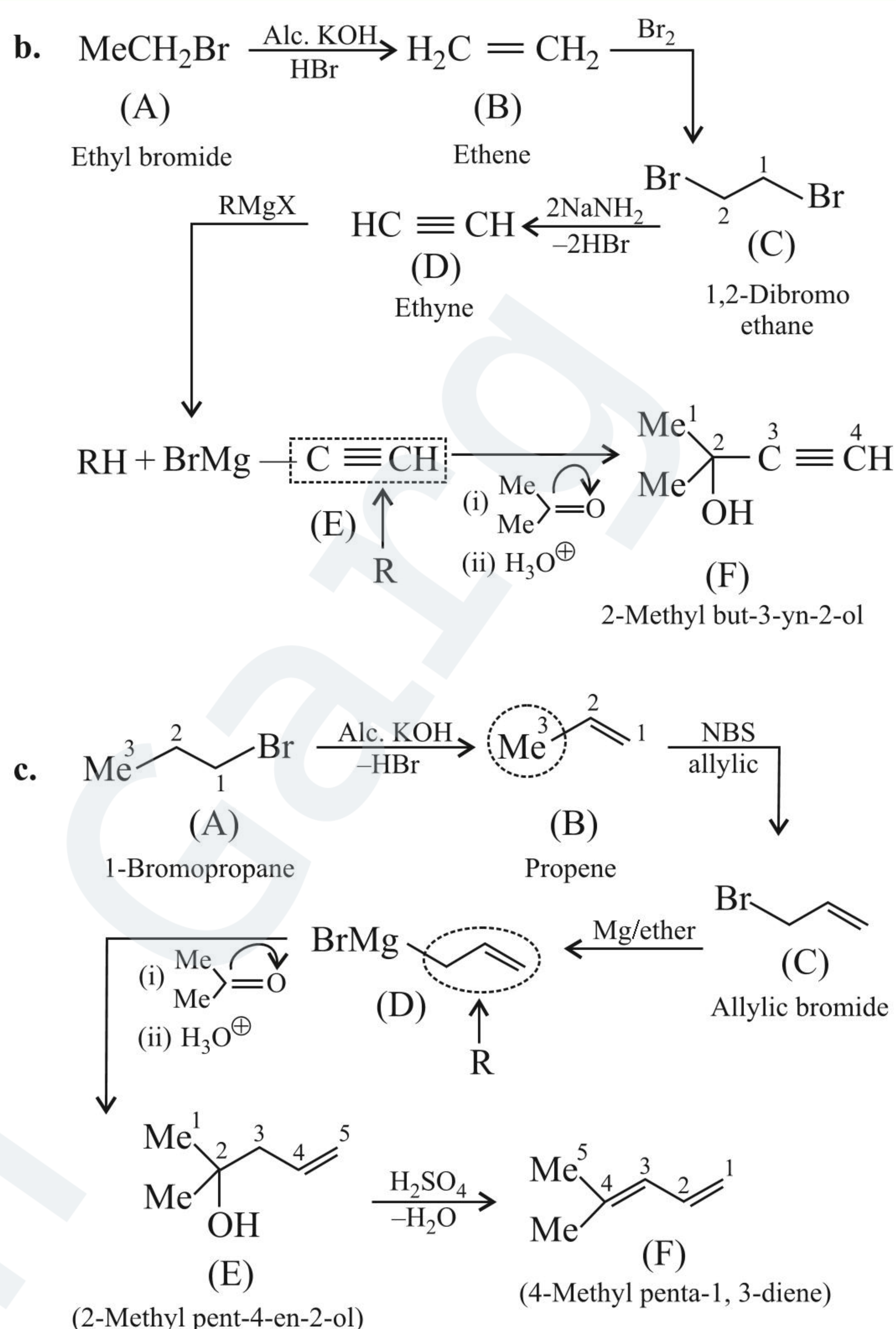
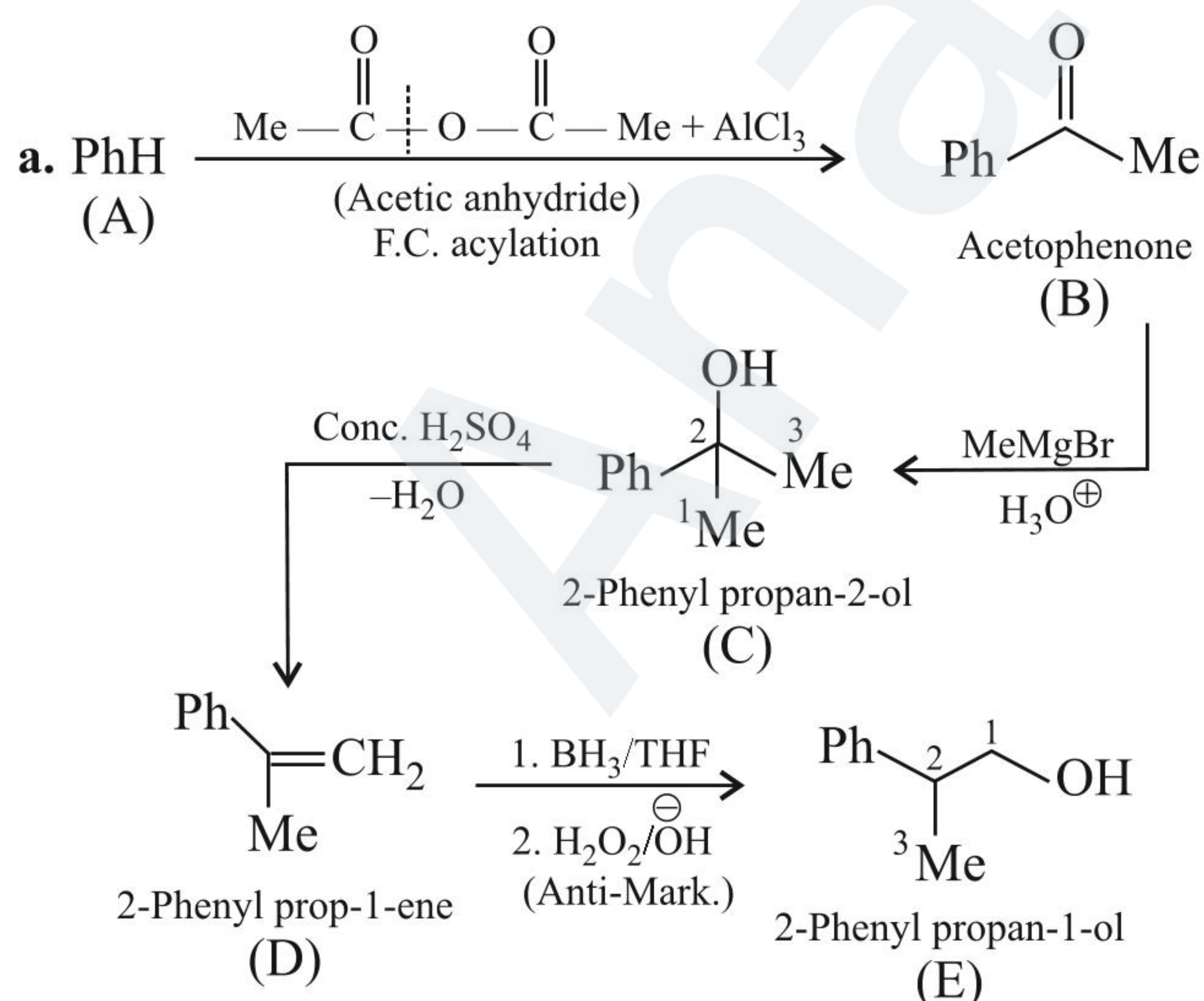
The D of ROD rapidly exchanges for H of H₂O.

ILLUSTRATION 4.9

Complete the following reactions:



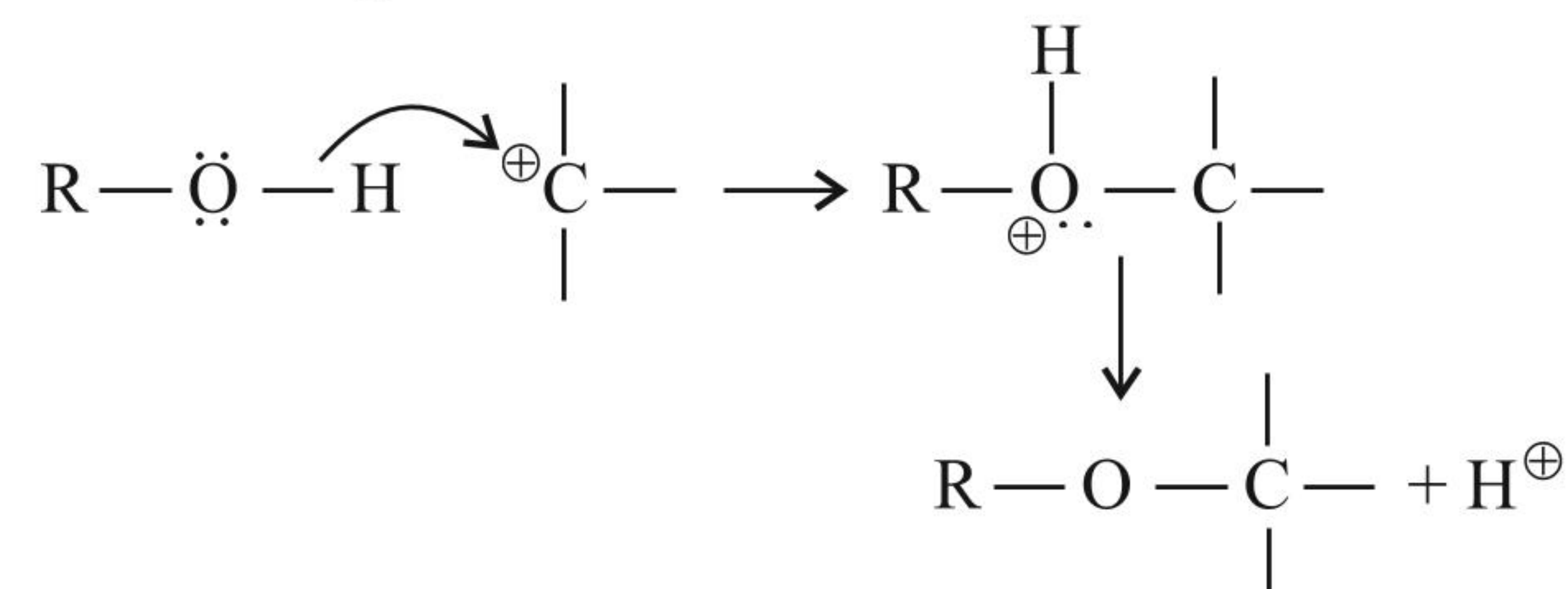
Sol.



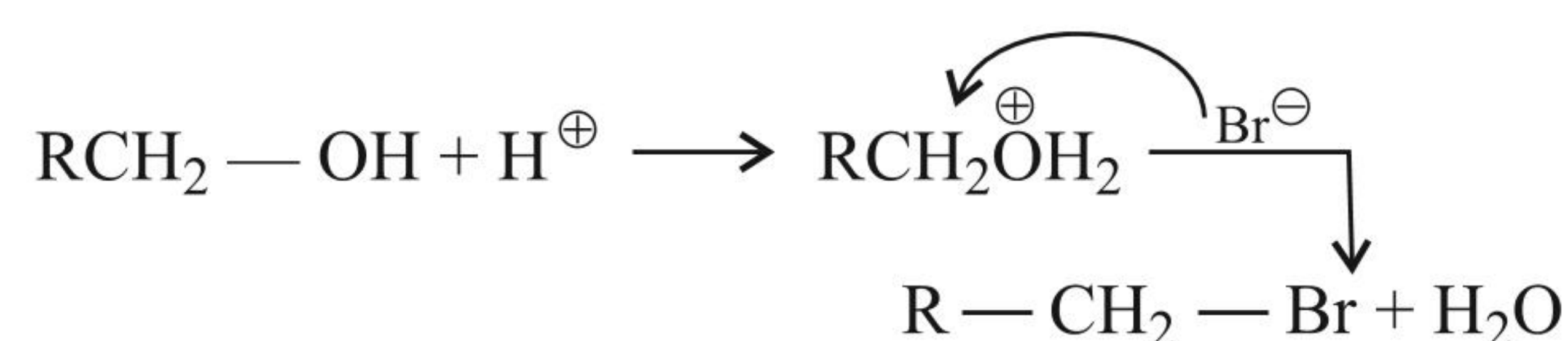
4.11 CHEMICAL REACTIONS OF ALCOHOLS

Alcohols react both as nucleophiles and electrophiles. When they react as nucleophile, (O—H) bond is broken and when they react as electrophile, (C—O) bond is broken. For example:

i. ROH as nucleophile:

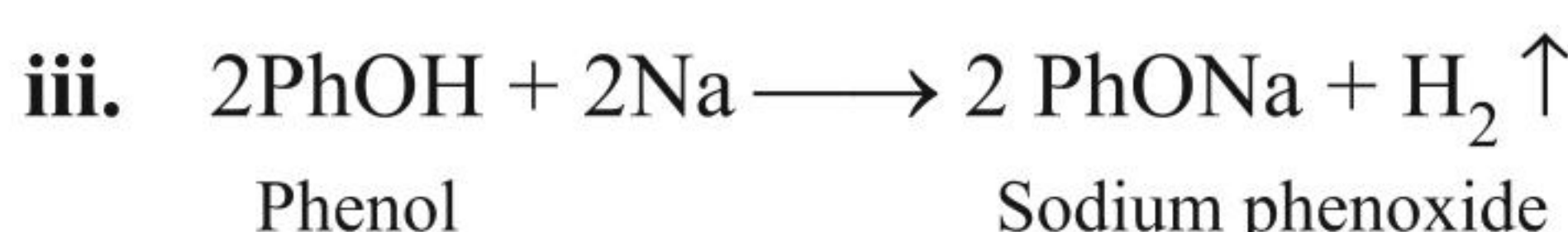
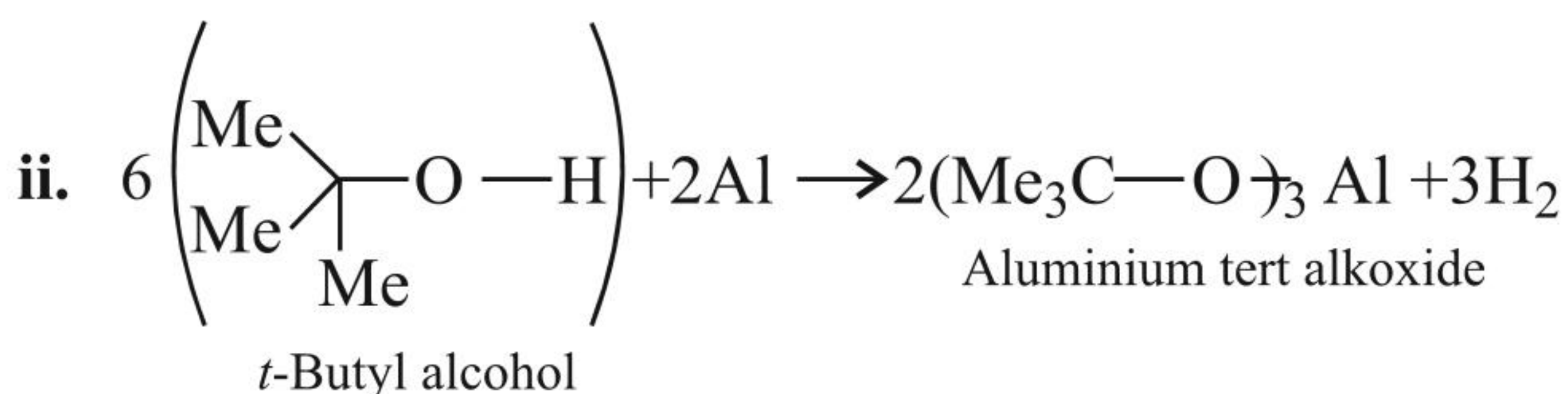
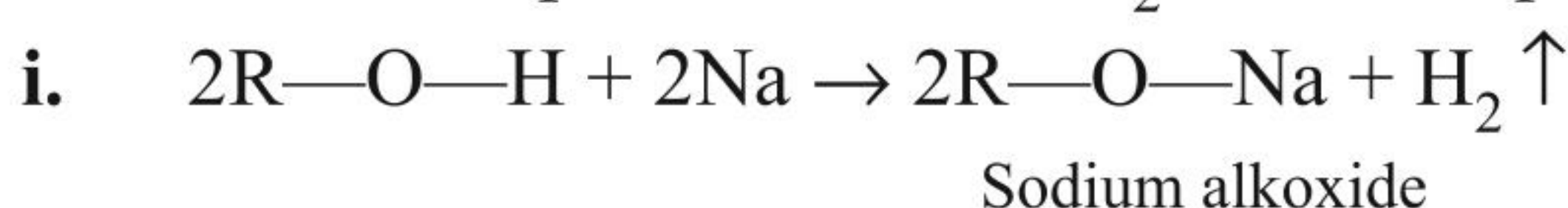


ii. R⁺OH₂ (protonated alcohol) as electrophile:

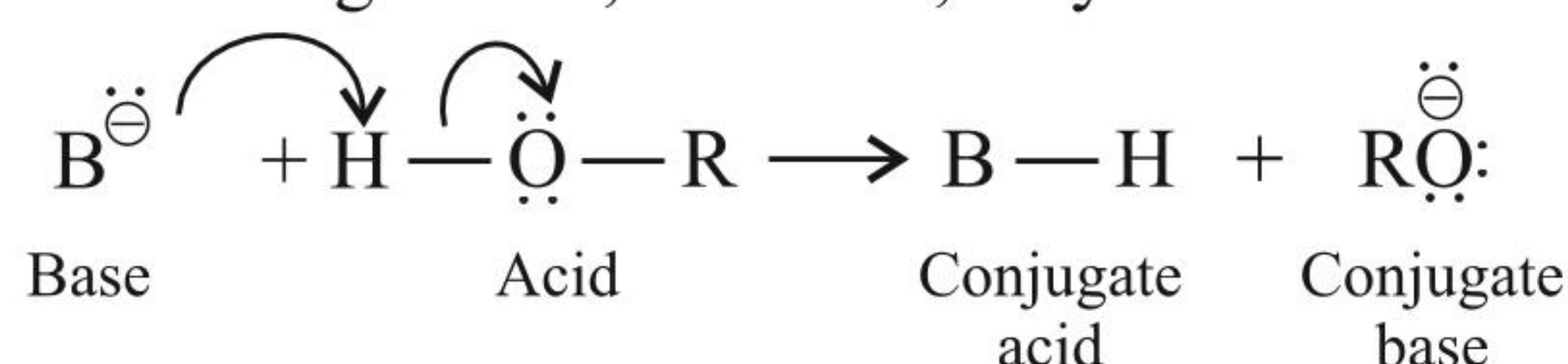


4.11.1 REACTIONS INVOLVING CLEAVAGE OF (O—H) BOND

a. **Reaction with metals:** ROH and ArOH react with active metals such as Na, K, and Al to give corresponding alkoxides/phenoxides and H₂. For example,



Thus ROH and ArOH are acidic in nature by donating a H⁺ to a stronger base; therefore, they act as Bronsted base.



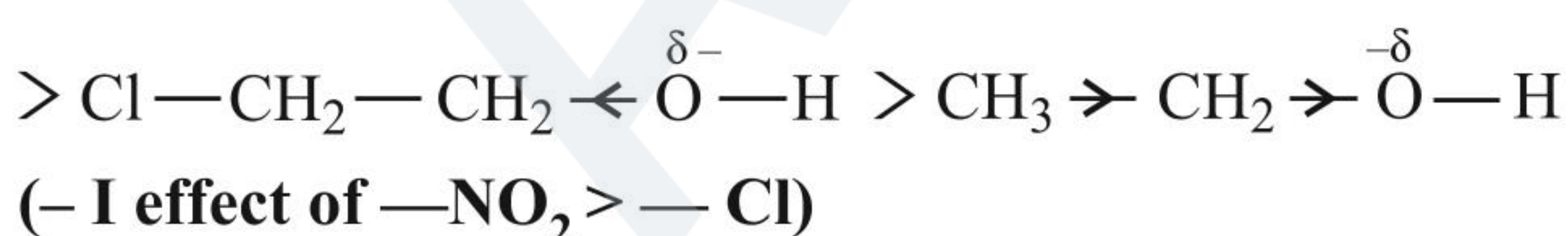
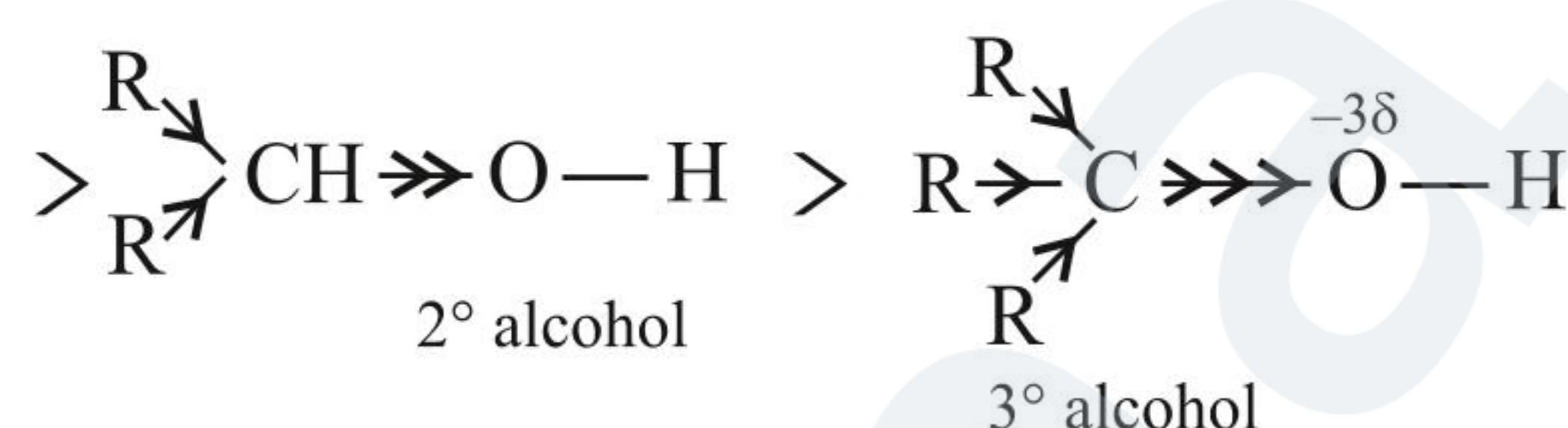
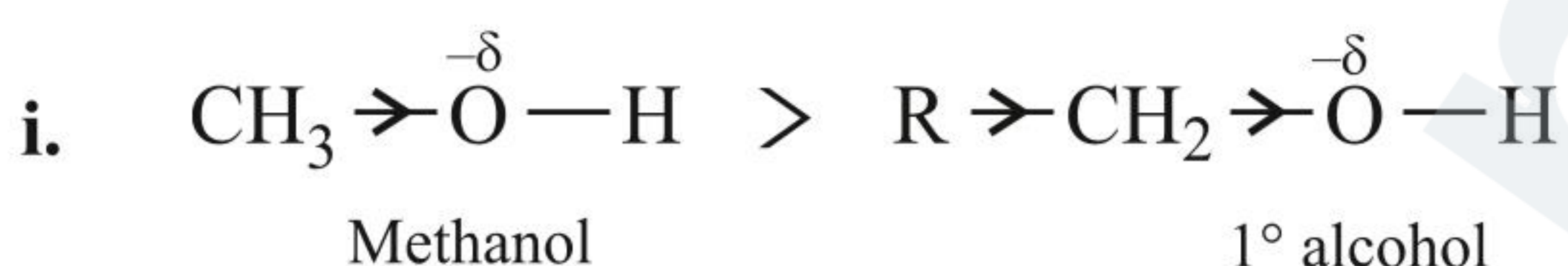
4.11.2 Acidity of Alcohols

The acidic character of alcohols is due to the polar nature of (O—H) bond. An \bar{e} -donating R (alkyl) group increases the \bar{e} density on O atom which decreases the polarity of (O—H) bond and acid strength decreases. In general, +I effect decreases and −I effect increases the acid strength of alcohols.

Therefore, acid strength of 1° > 2° > 3° alcohols.

Note: Higher the K_a or lower the pK_a value, stronger is the acid.

Decreasing acid strength or decreasing K_a or increasing pK_a value of the following:

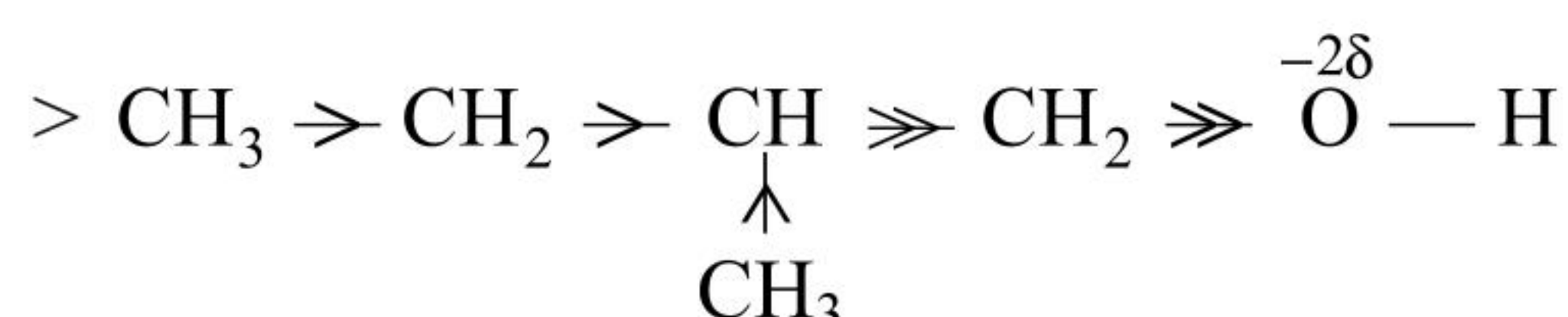
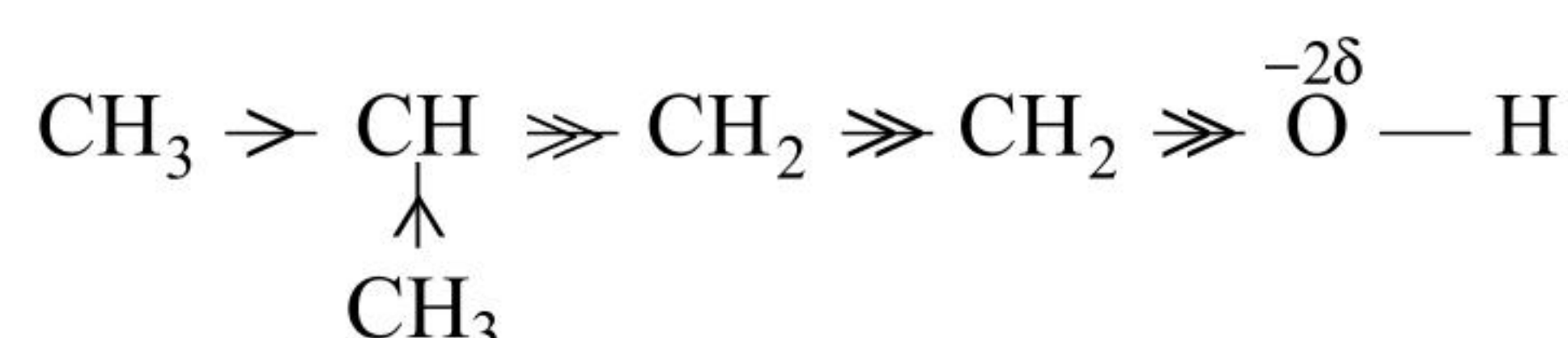
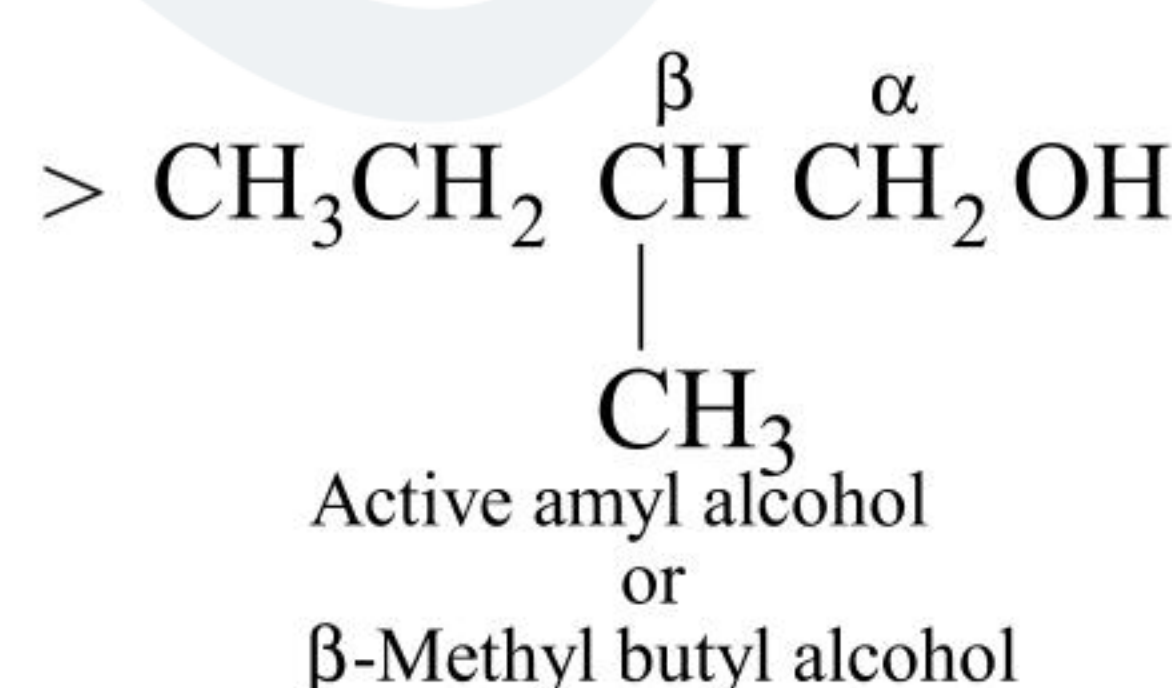
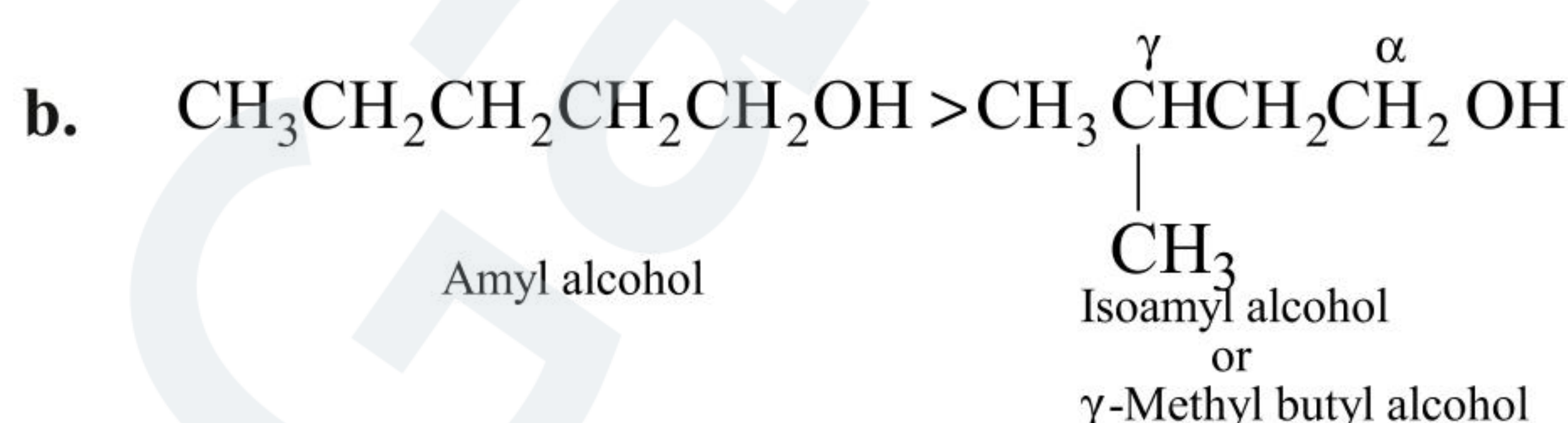
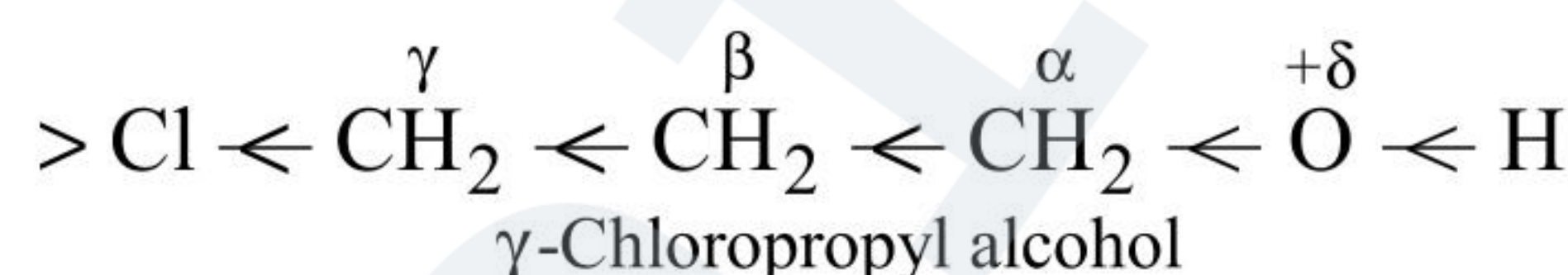
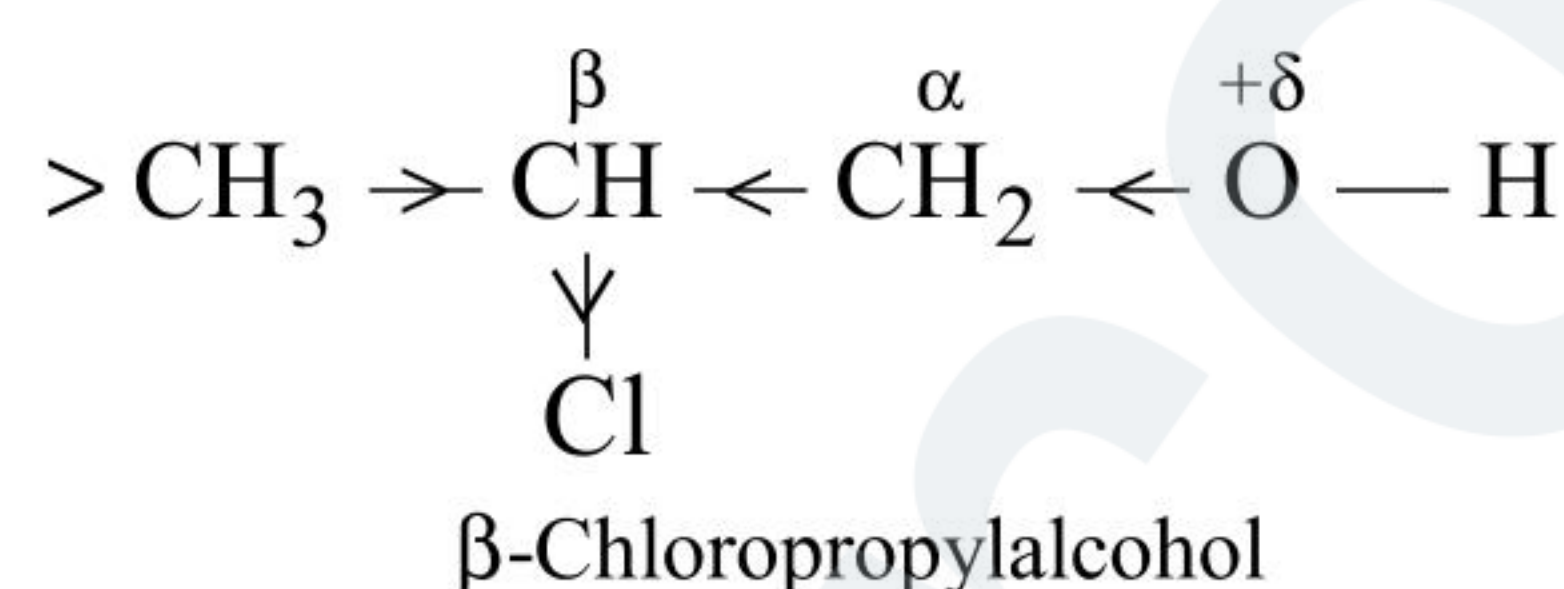
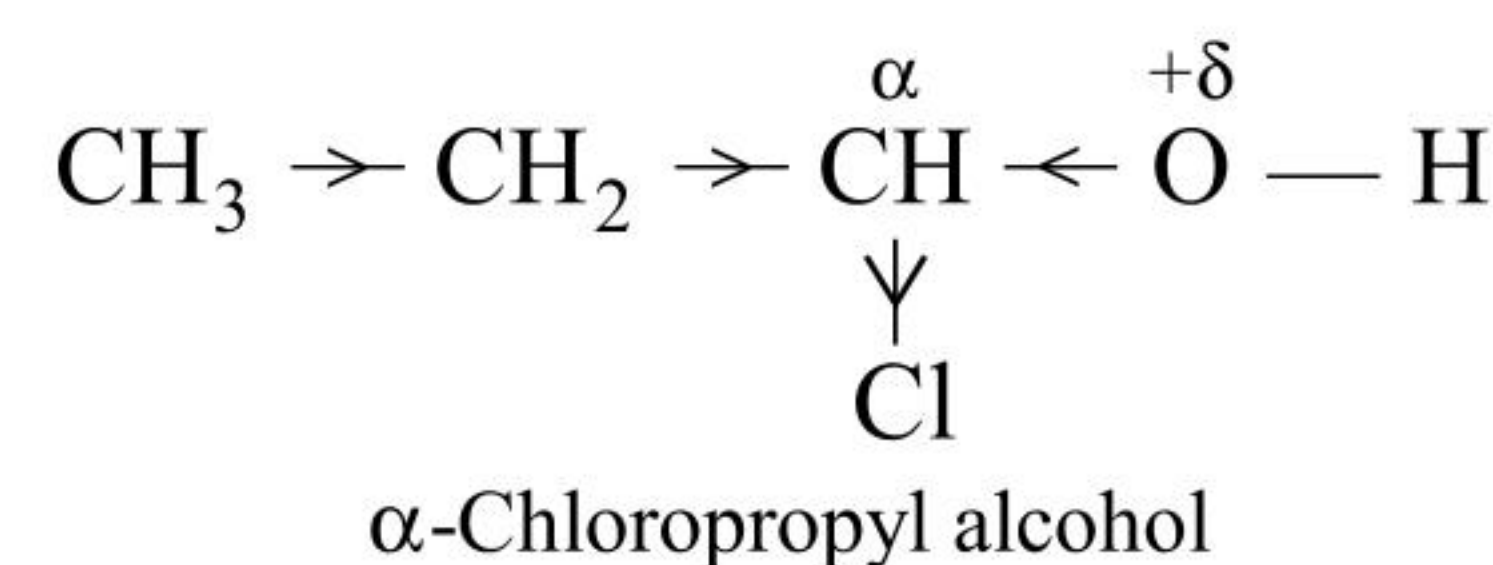
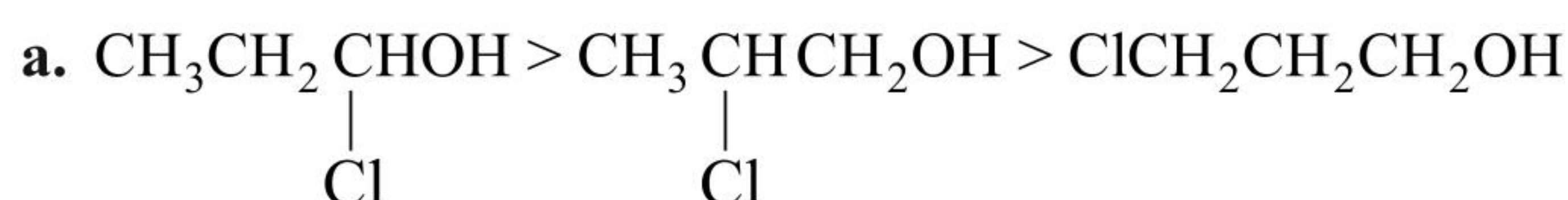


iii. If −I effect is short distance operating (i.e., nearer) from the source (e.g., (—OH) group), the acid is stronger and *vice versa*.

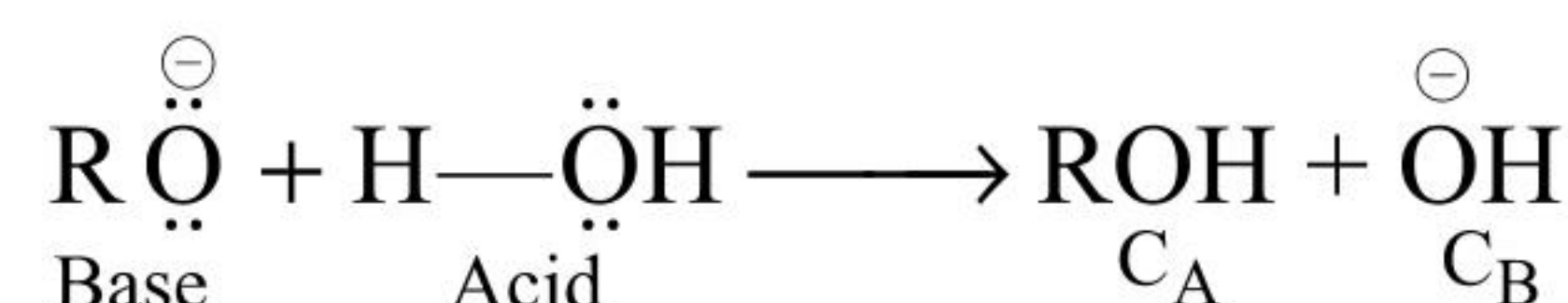
iv. Similarly, if +I effect is long distance operating (i.e., far away) from the source (e.g., (—OH) group), the acid is stronger and *vice versa*.

For example,

Decreasing acid strength (decreasing K_a or increasing pK_a value):



v. Alcohols (except methanol) are weaker acids than H₂O because H₂O is a better H⁺ donor and R[−]O[−] (alkoxide ion) is a better H⁺ acceptor than OH[−] ion. So RO[−] is a stronger base (e.g., EtO[−] ethoxide ion) than NaOH.



Decreasing acidic order:



pK_a value:



Basic and nucleophilicity order:



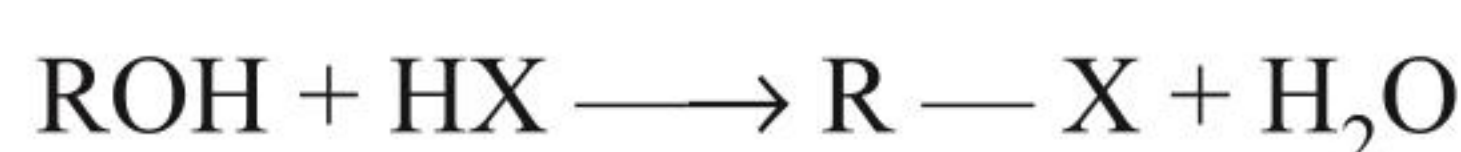
Stronger the acid, weaker is its C_B. Nucleophilicity and basic order are same when nucleophilic center is same.

4.11.3 REACTIONS INVOLVING CLEAVAGE OF (C—O) BOND IN ALCOHOLS

The reactions involving cleavage of (C—O) bond occur only in alcohols. Phenols show such type of reactions only with Zn.

a. Reactions with hydrogen halide:

ROH reacts with HX to form RX.

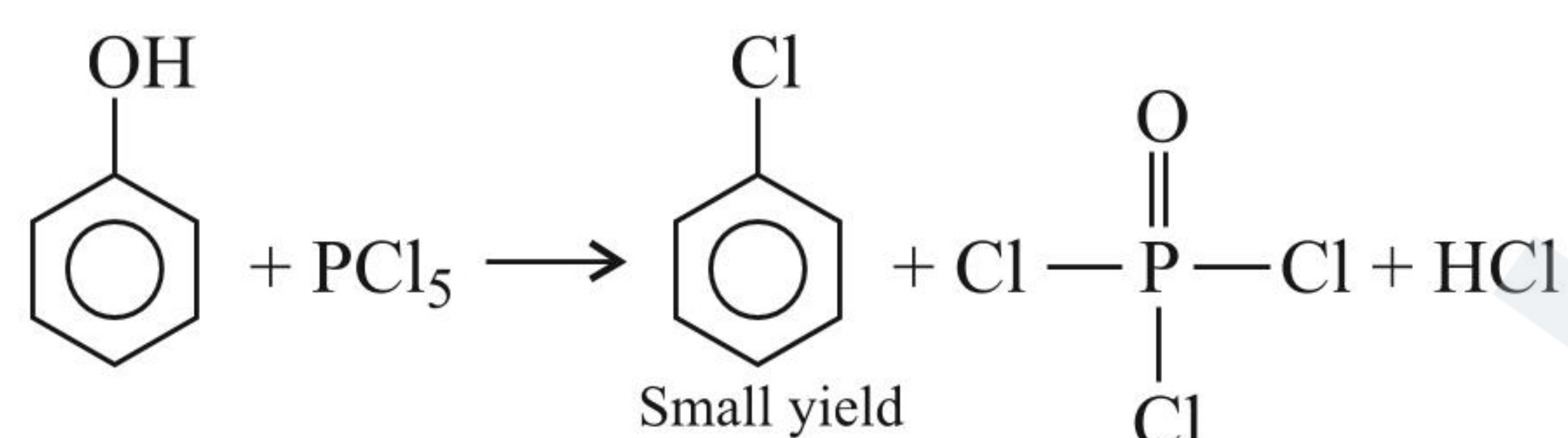
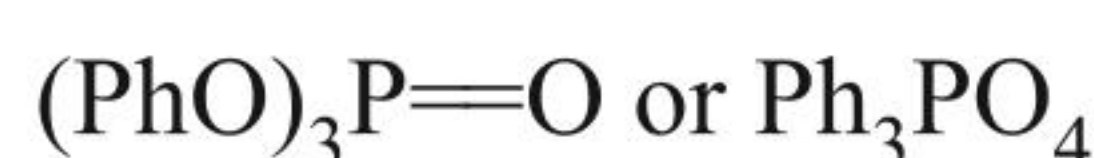


The 1°, 2°, 3° alcohols are distinguished from one another by Lucas test and by Victor–Meyer's test (see Chapter 2).

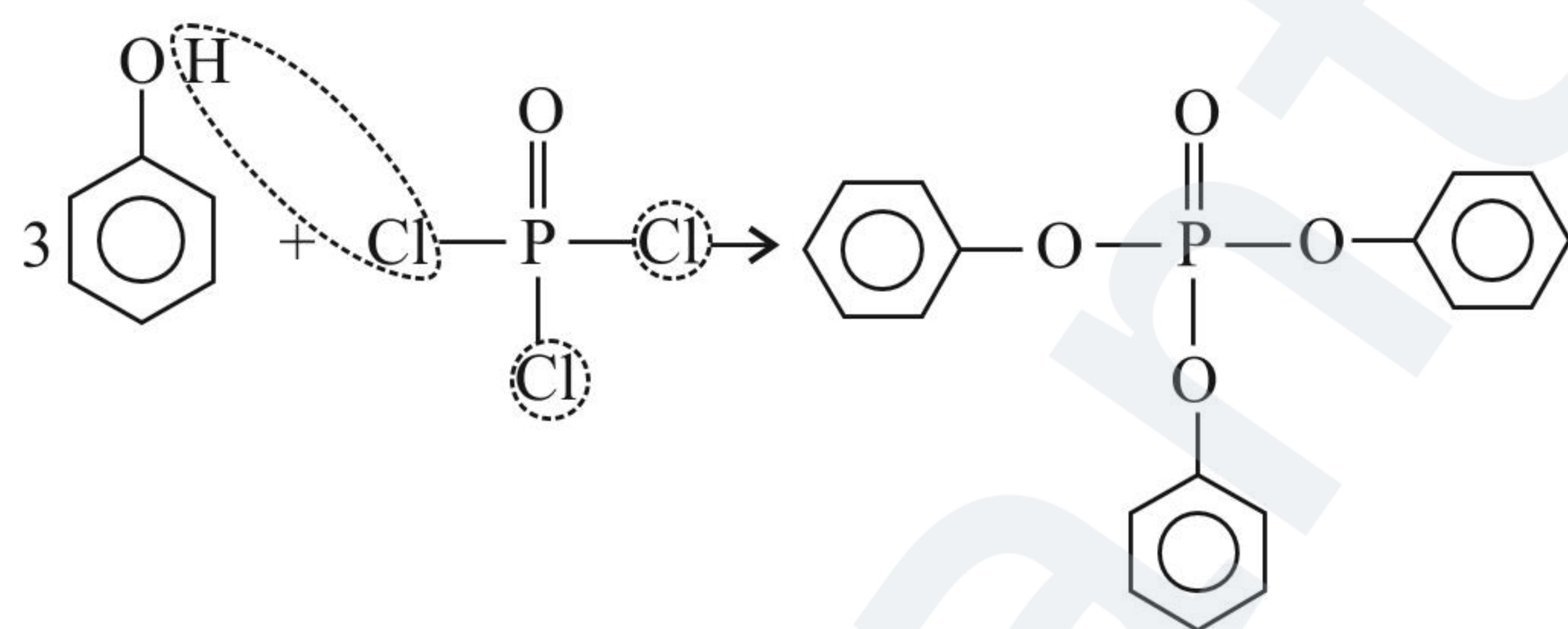
b. Distinguish test between alcohols and phenols:

c. Reaction with PX₃: Alcohols are converted to RBr with PBr₃.

The (—OH) group of phenol, unlike that of alcohol, is difficult to replace by a halogen, e.g., halogen acids have no action and PX₃ yields only phosphorous esters. **Phenol reacts with PCl₅ or PBr₅**, when the (—OH) group of phenol is replaced by halogen atom. The yield of chloro- or bromo-benzene is small, the main product being triphenyl phosphate.

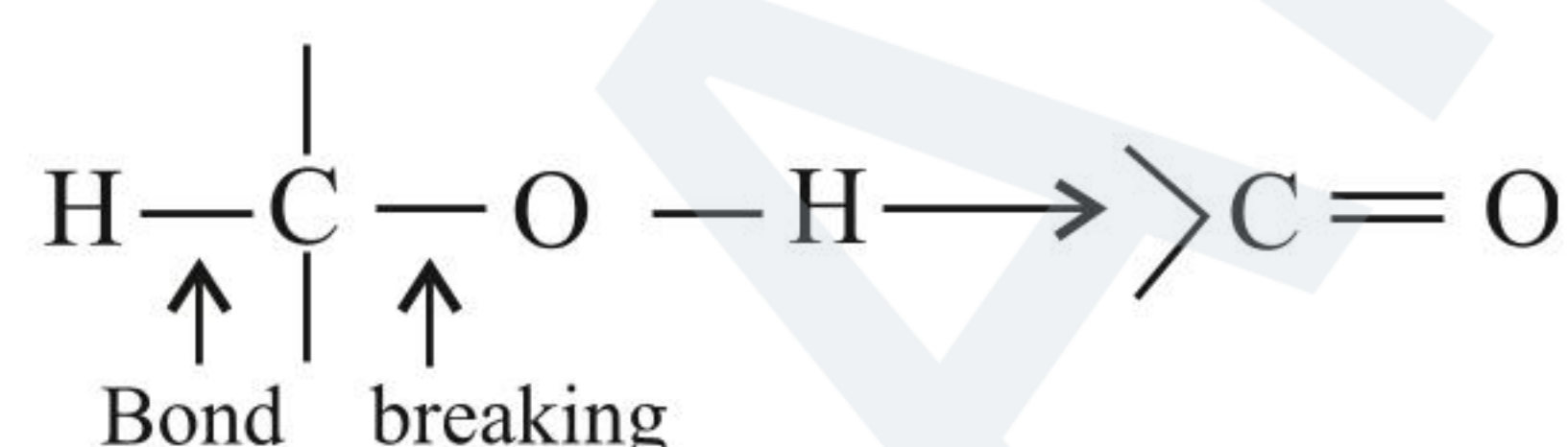


Phenol further reacts with POCl₃ to give Ph₃PO₄.



d. Oxidation of alcohols:

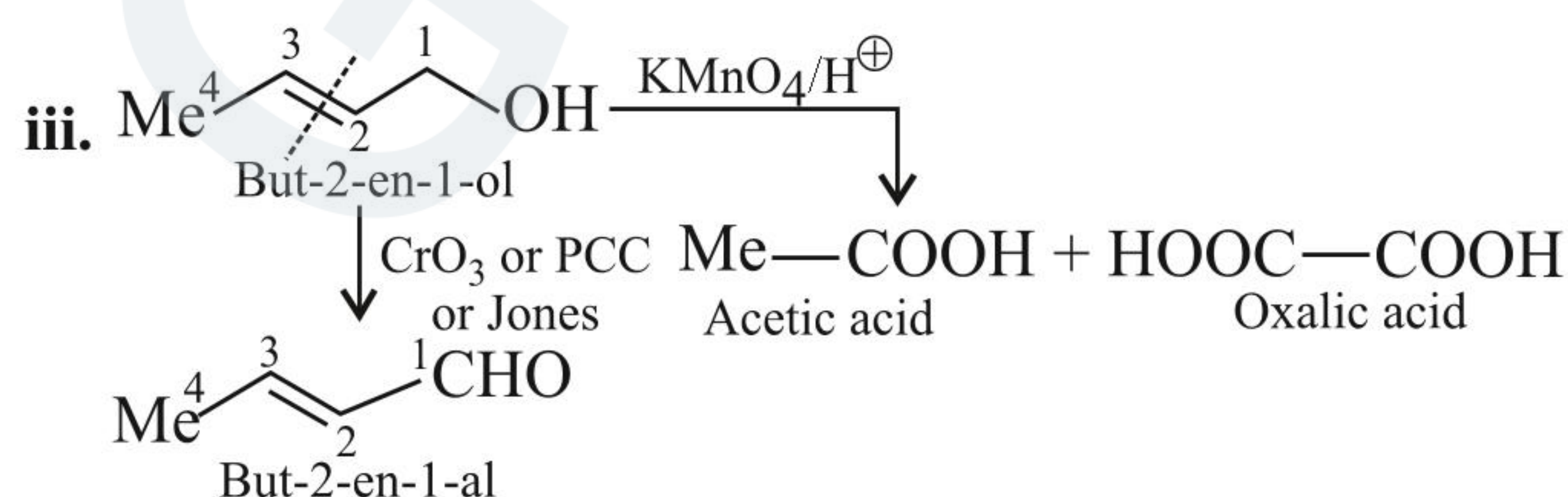
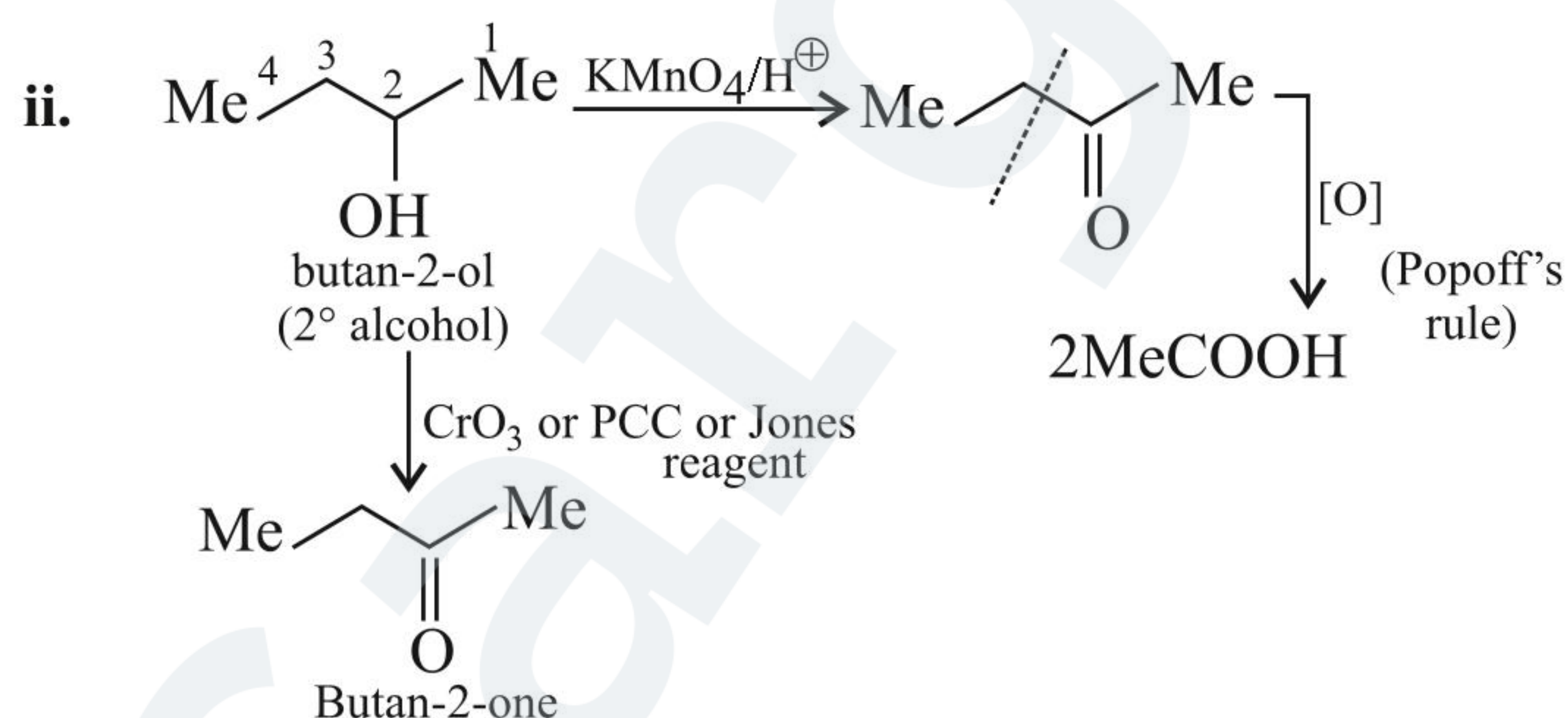
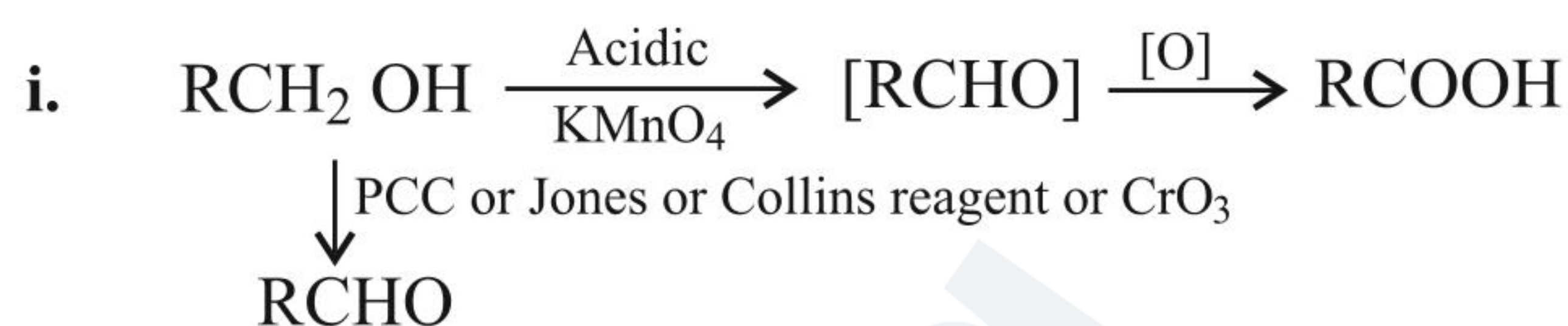
Oxidation of ROH involves the cleavage of (O—H) and (C—H) bonds to form $\left(\text{>C}=\text{O}\right)$ bond.



Such reactions are also called dehydrogenation reactions because H₂ is lost from an alcohol molecule. Strong oxidising agents such as acidic KMnO₄ or acidic K₂Cr₂O₇ oxidise 1° ROH first to an aldehyde and then to carboxylic acids. Further, 2° alcohols are oxidised to ketones and 3° alcohols do not undergo oxidation, but under drastic conditions such as strong oxidising agents (KMnO₄) and at high temperatures cleavage of (C—C) bonds takes place and a mixture of RCOOH containing lesser number of C atoms is formed. 1° ROH can

be converted upto aldehyde stage either by the use of CrO₃ in anhydrous medium or with PCC or with Jones reagent.

Examples:

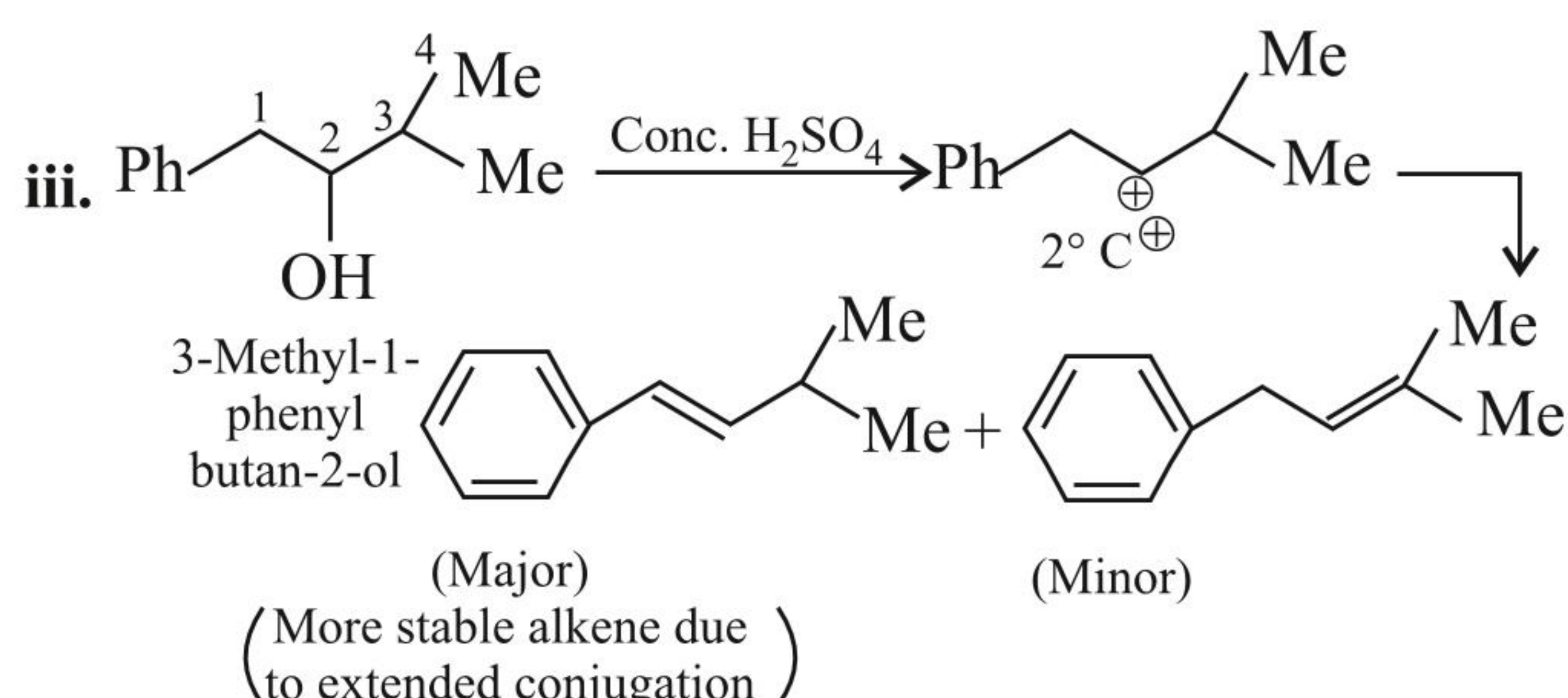
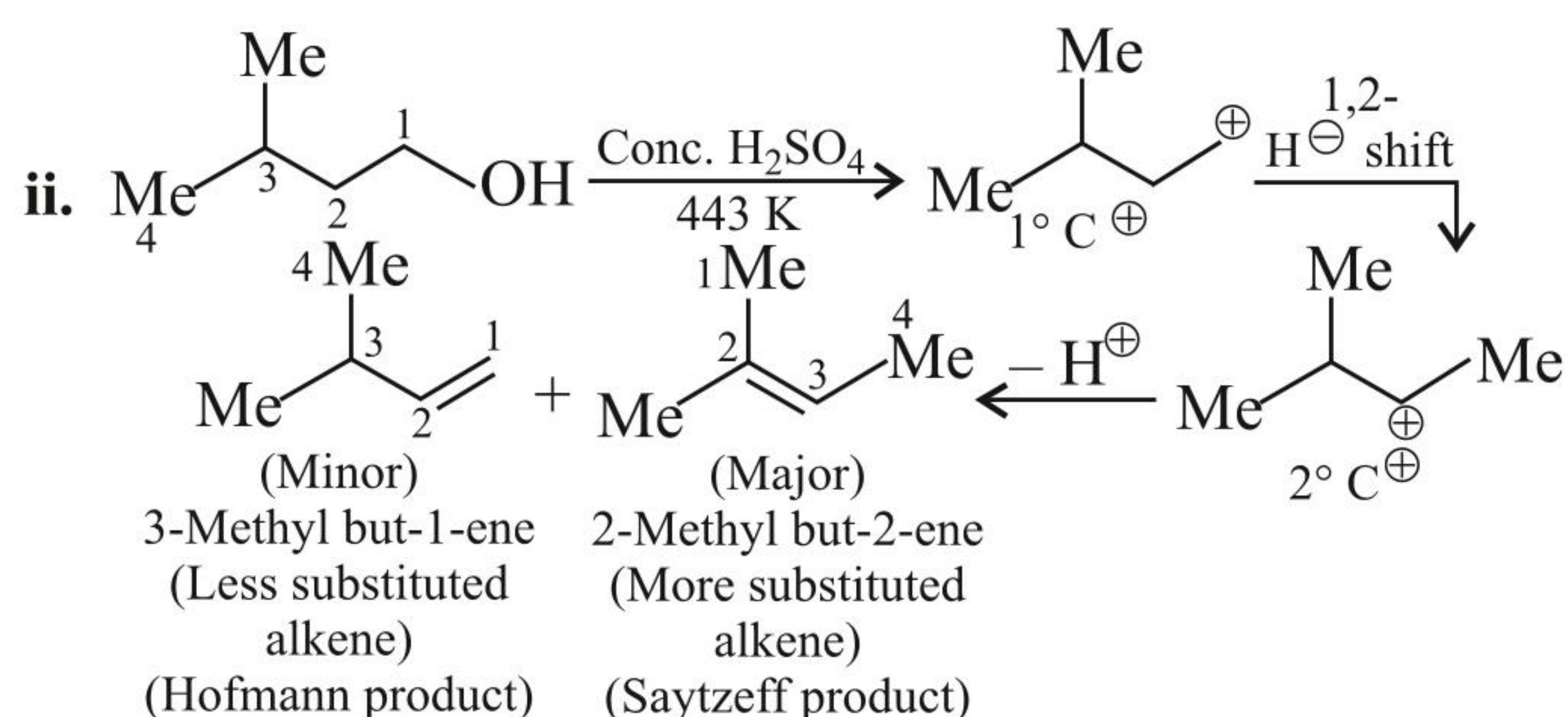
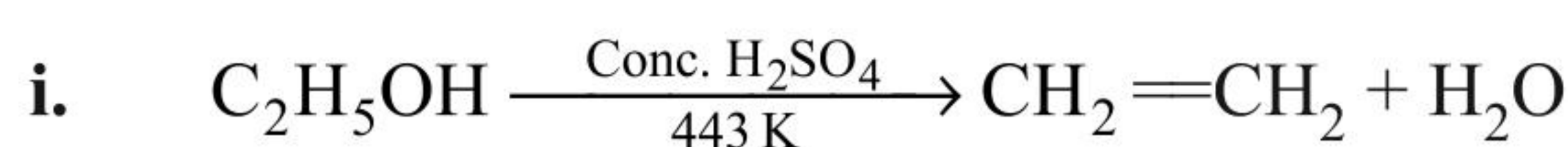


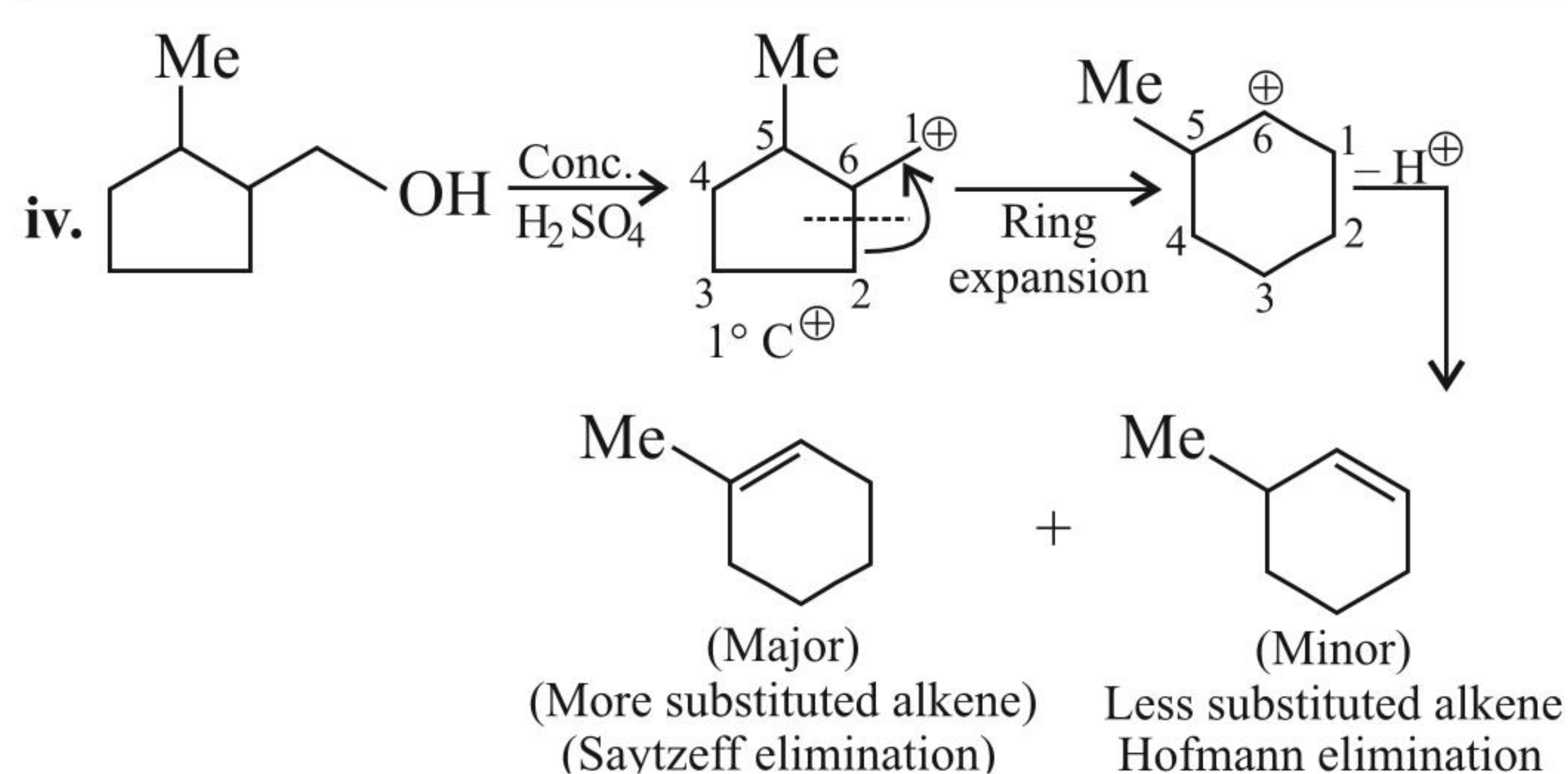
e. Dehydrogenation with hot copper at 573 K:

1° alcohols with hot Cu at 573 K give aldehydes, 2° alcohols give ketones, and 3° alcohols undergo dehydration to give alkenes.

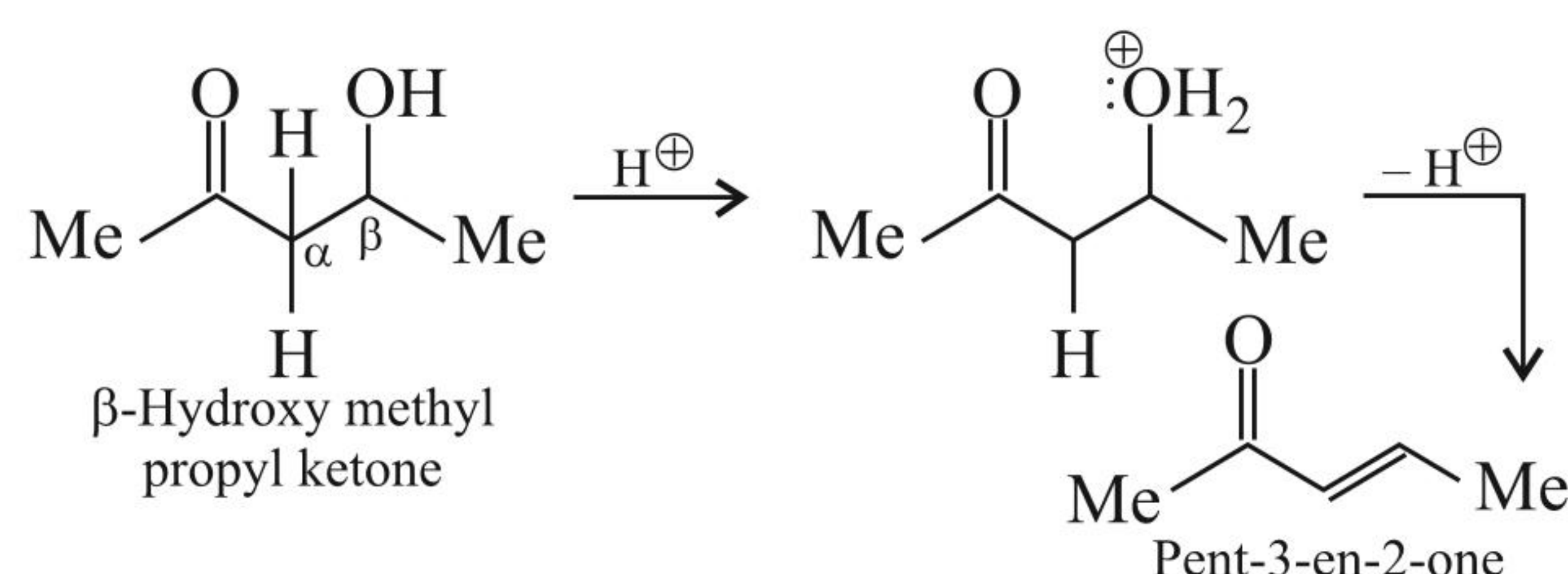
4.12 DEHYDRATION

Alcohols on reaction with conc. H₂SO₄ or H₃PO₄ or anhydrous ZnCl₂ or alumina (Al₂O₃) give alkenes, e.g.,

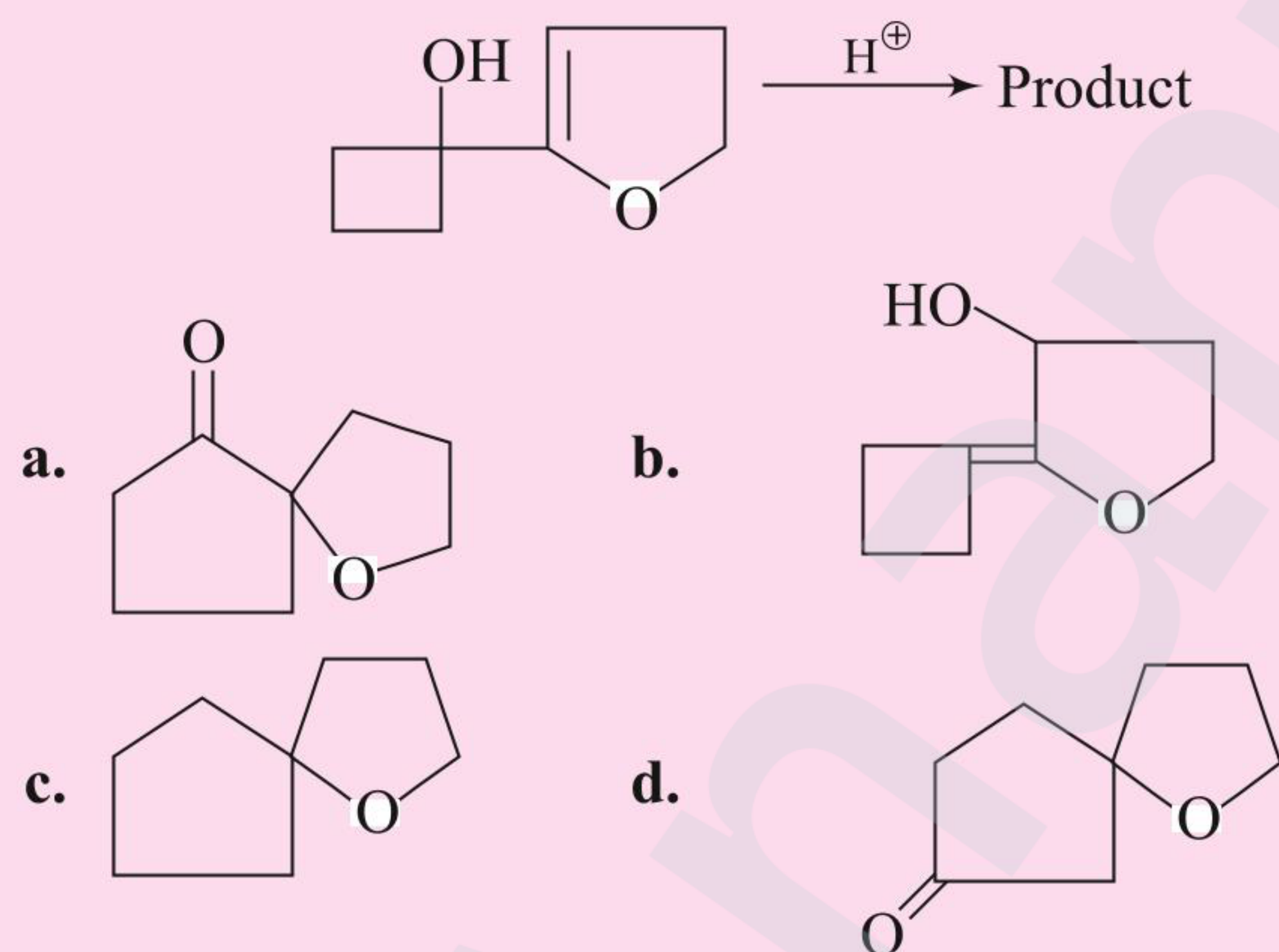


**Ease of Dehydration:**

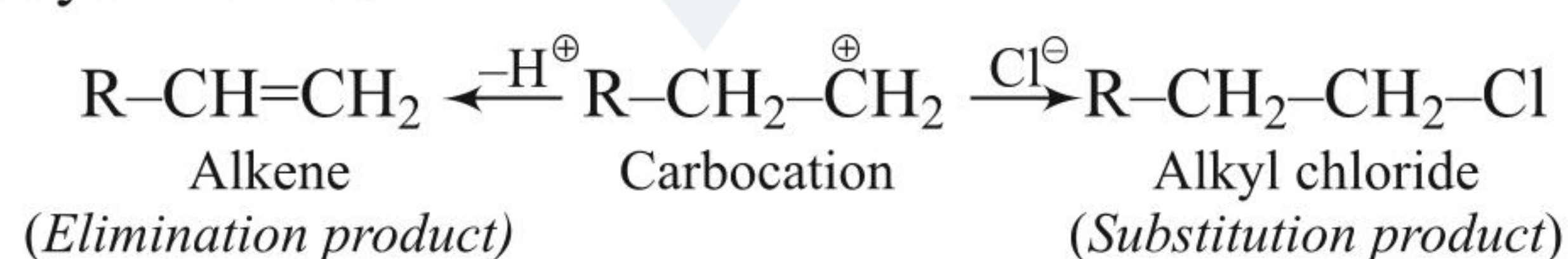
- $3^\circ > 2^\circ > 1^\circ$ alcohols
- β -Hydroxy aldehydes or ketones readily undergo dehydration giving α,β -unsaturated carbonyl compound.

**ILLUSTRATION 4.10**

- Explain why dehydration of alcohols to alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 .
- Identify the major product



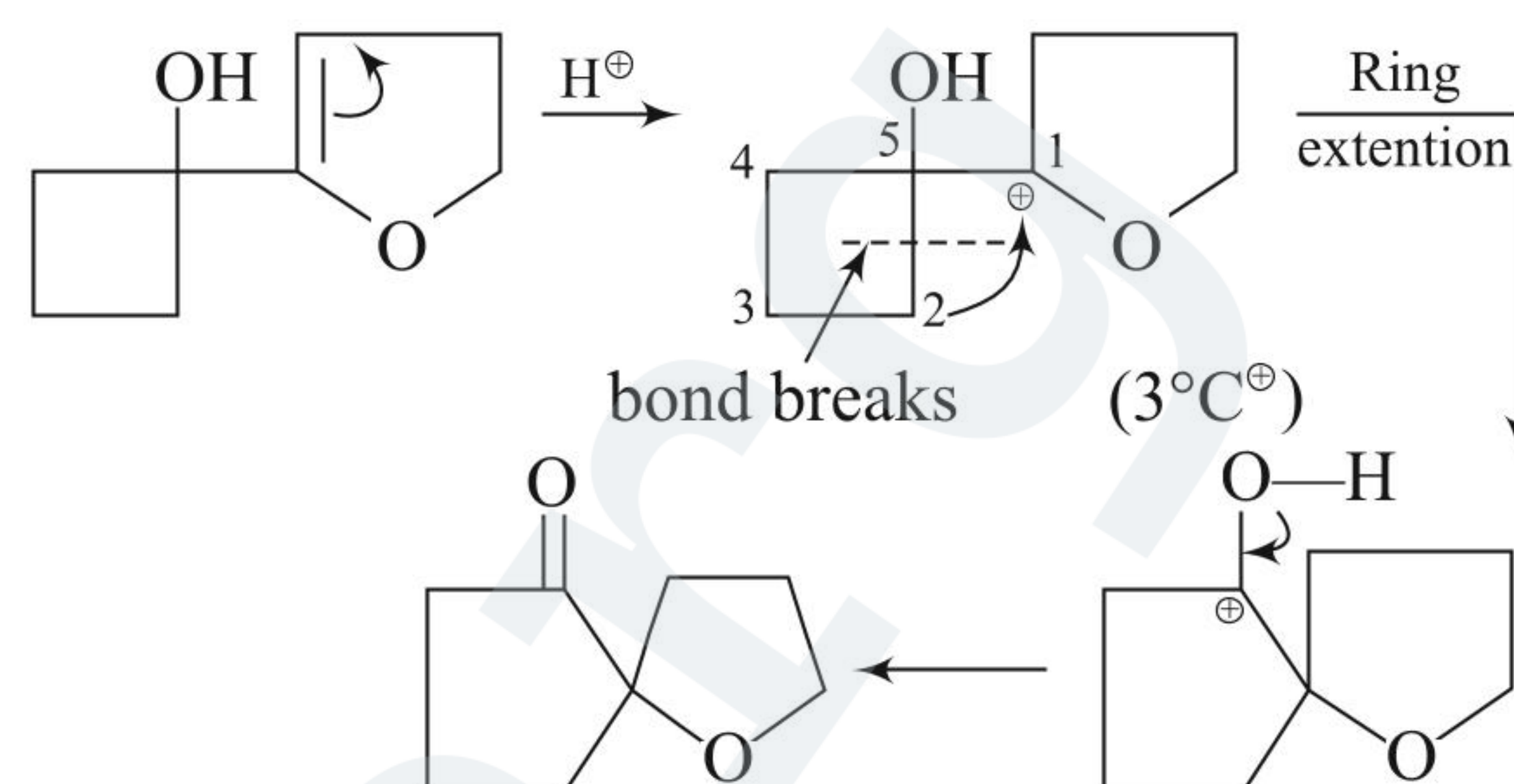
Sol. (I) Dehydration of alcohols to form alkenes occurs through carbocation intermediates. If HCl is used, then chloride (Cl^-) ion being a *good nucleophile* bring about substitution reaction to give an alkyl chloride.



If H_2SO_4 is used, then the bisulphate ion HSO_4^- being *non-nucleophilic* cannot bring about the substitution reaction. Instead the carbocation loses a proton to form an alkene. Conc HNO_3 is not used because it being a strong oxidizing agent, preferentially

bring about the oxidation of alcohols first to aldehydes or ketone and then to the carboxylic acids. Thus *dehydration of alcohols to form alkenes is always carried out with such strong acids* (e.g. H_2SO_4 , H_3PO_4 , KHSO_4) which have non-nucleophilic anions.

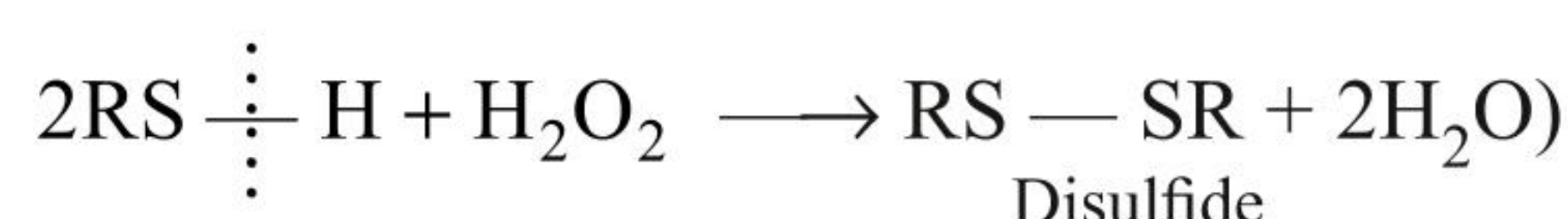
(II) Protonation first occurs at double bond rather than at ($-\text{OH}$) group



4.13 COMPARISON OF ACIDIC CHARACTER OF THIOLS AND ALCOHOLS

Thiols or mercaptans (RSH) ($K_a \approx 10^{-11}$) are more acidic than alcohols ($K_a \approx 10^{-17}$). This is due to:

- Size of $\text{S} > \text{O}$ and S is more polarisable than O atom.
- Bond dissociation energy of ($\text{S}-\text{H}$) bonds of thiols (~ 330 kJ) is much less than that of ($\text{O}-\text{H}$) bond of alcohols (~ 420 kJ).
- In alcohols, oxidation takes place at the weaker ($\text{C}-\text{H}$) bond (~ 360 kJ) rather than at the stronger ($\text{O}-\text{H}$) bond.
- Thiols undergo oxidative coupling reaction with mild oxidising agent, whereas alcohols do not undergo such reaction.



- Sulphur compounds are powerful nucleophile and compounds containing (SH) groups are stronger acid than their oxygen analogues.

Therefore, $\text{C}_2\text{H}_5\text{S}^-$ is stronger nucleophile than $\text{C}_2\text{H}_5\text{O}^-$ ion.

4.14 ACIDITY OF PHENOLS

The reaction of phenol with Na , K , Al , and NaOH indicates its acidic nature. Reaction of phenol with aqueous NaOH indicates that phenols are stronger acids than alcohols and H_2O .

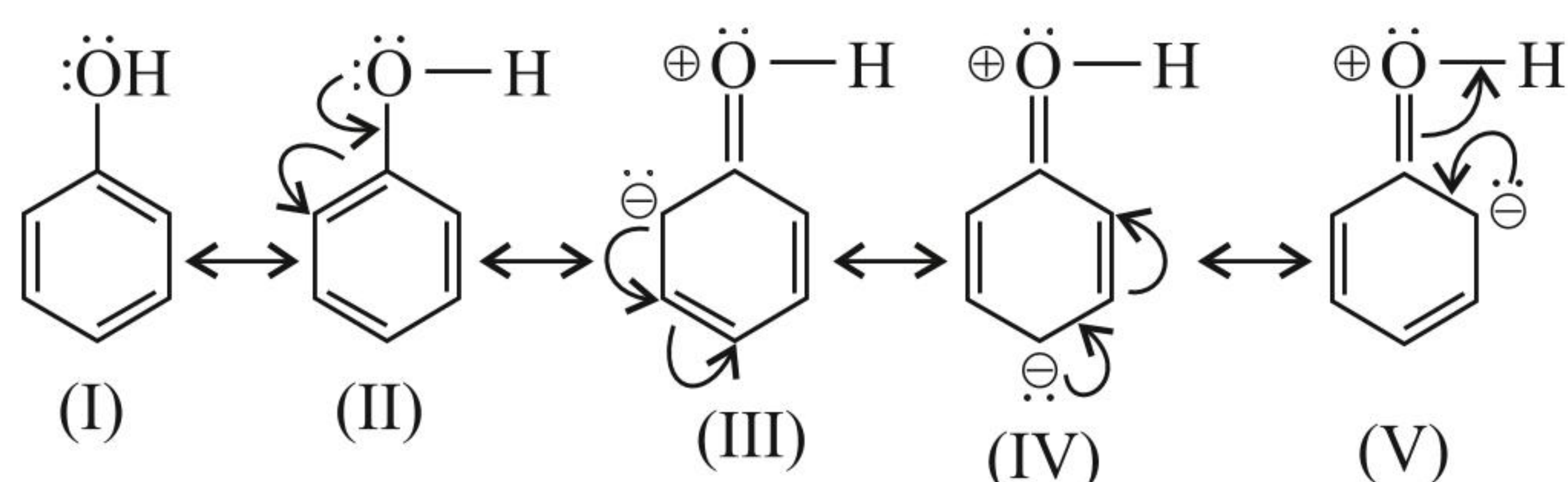
- In substituted phenols, the presence of \bar{e} -withdrawing groups (e.g., $-\text{NO}_2$, $-\text{SO}_3\text{H}$, or $-\text{X}$) increases the acidic strength. This effect is more pronounced when such a group is present at *o*- and *p*-positions. It is due to the effective delocalisation of negative charge in phenoxide ion.

The \bar{e} -donating groups (e.g., $-\text{R}$, $-\text{OR}$) do not favour the formation of phenoxide ion, and thus decreases the acid strength.

- Effect of resonance on acidic character of phenols:**

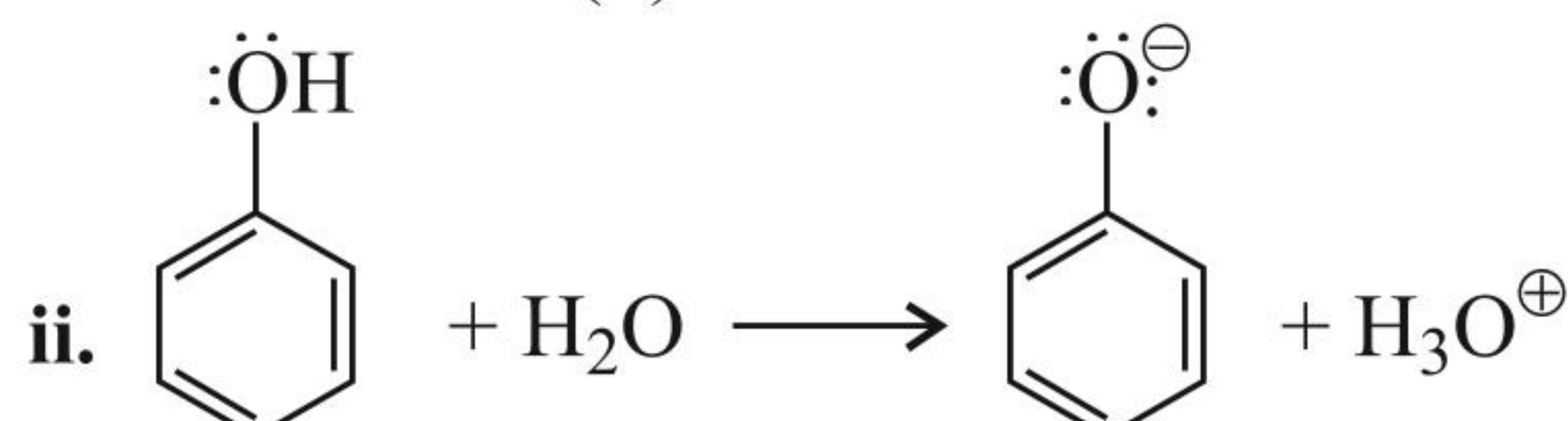
Phenols are more acidic than alcohols and cyclohexanols.

- Due to $+\text{M}$ effect (\bar{e} -donation effect) of ($-\text{OH}$) group, phenol is resonance-stabilised as shown below:

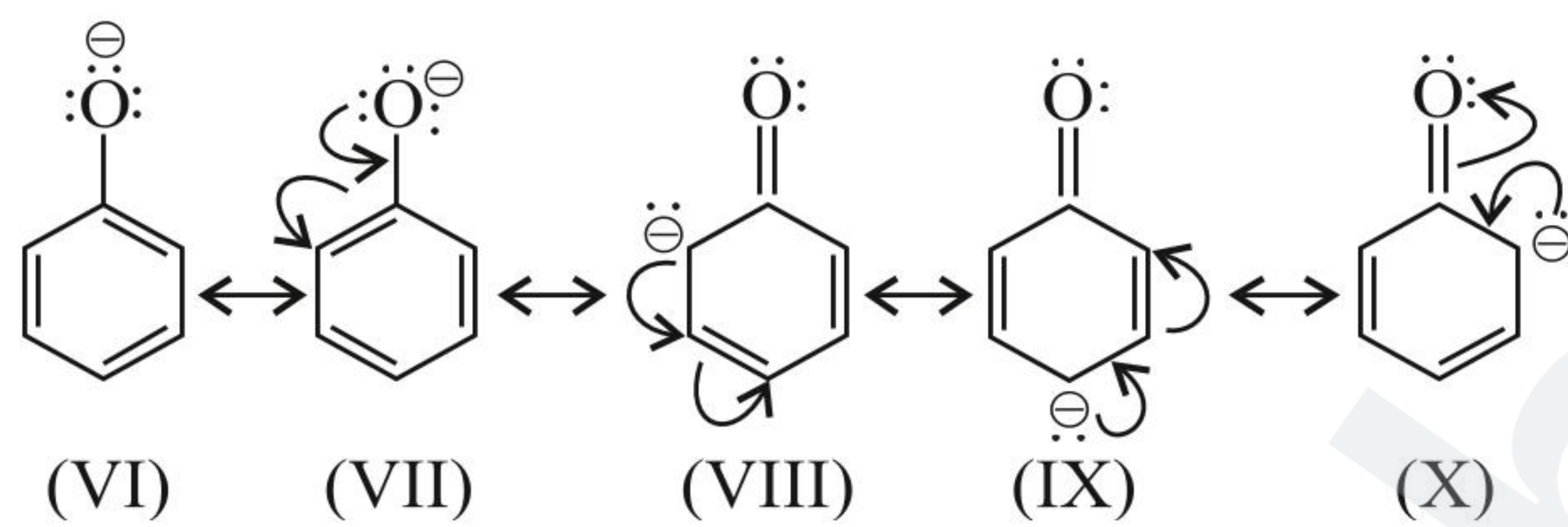


(Structures (III) to (V) involve charge separation and hence are less stable.)

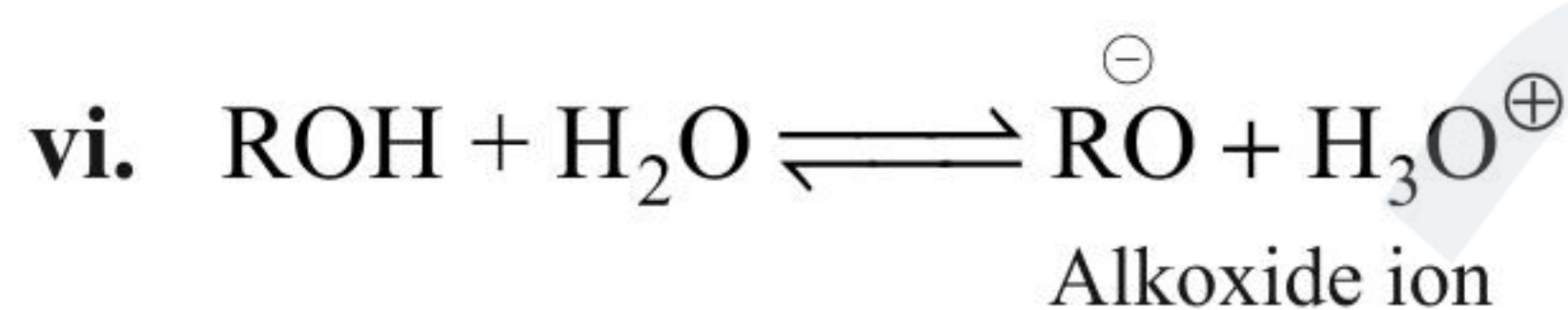
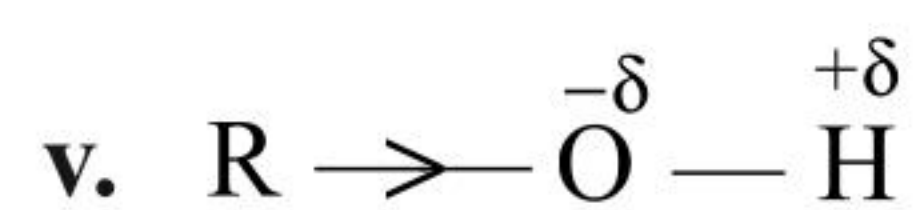
Due to resonance, oxygen atom of (—OH) group acquires a positive charge and hence attracts e^- pair of the (O—H) bond leading to the release of hydrogen atom as proton, as shown in (ii).



iii. Once the phenoxide ion is formed, it stabilises itself by resonance. Actually, phenoxide ion is more stable than phenol because phenol resonance structures have charge separation but phenoxide ion resonance structures have no charge separation.



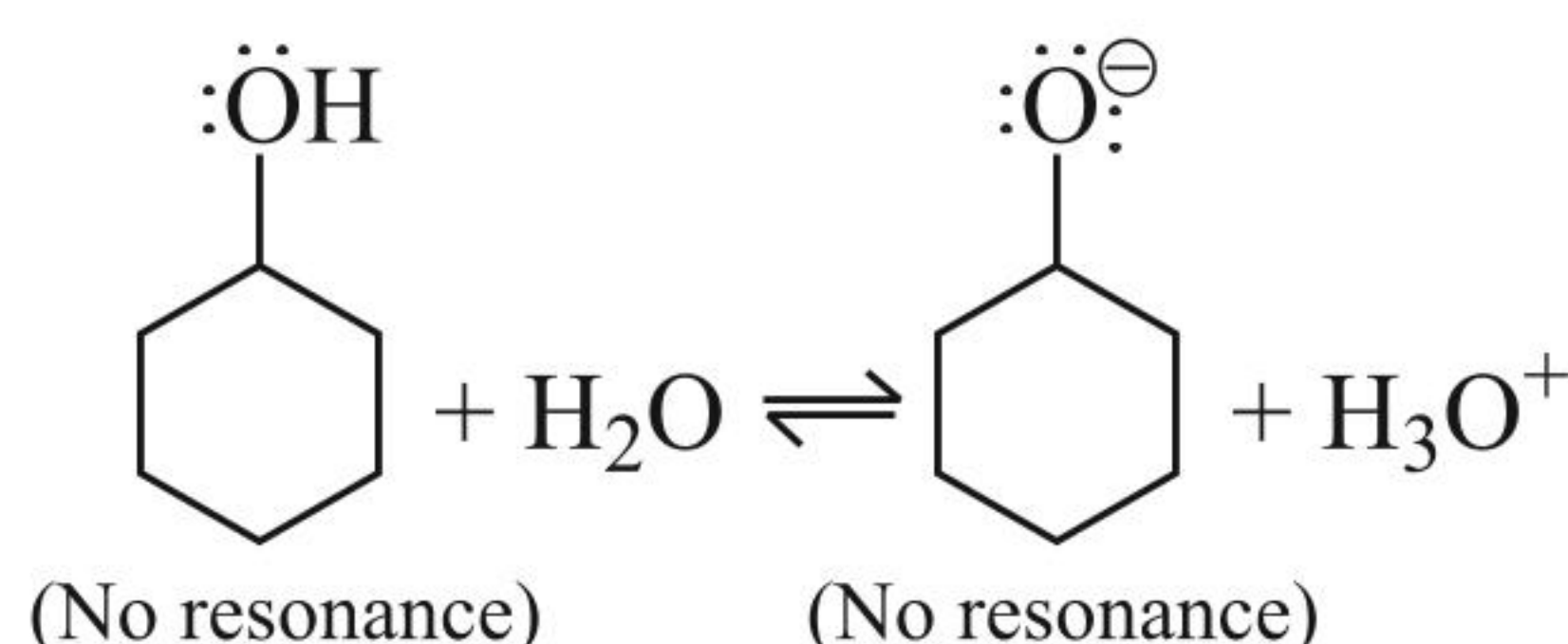
iv. In alcohols, resonance is not possible (due to the absence of conjugation of the lone pair of e^- 's of oxygen with a double bond). Moreover, due to +I effect (e^- -donating effect) of alkyl group in alcohol, oxygen atom of (O—H) group acquires a partial negative charge, and hence hydrogen atom is more firmly held to the oxygen atom and hence alcohols are weaker acids than phenols.



Moreover, once the alkoxide ion is formed, it is not resonance-stabilised. So, alkoxide is not stable and hence alcohols have practically no tendency to ionise to form alkoxide ion and hydrogen ions.

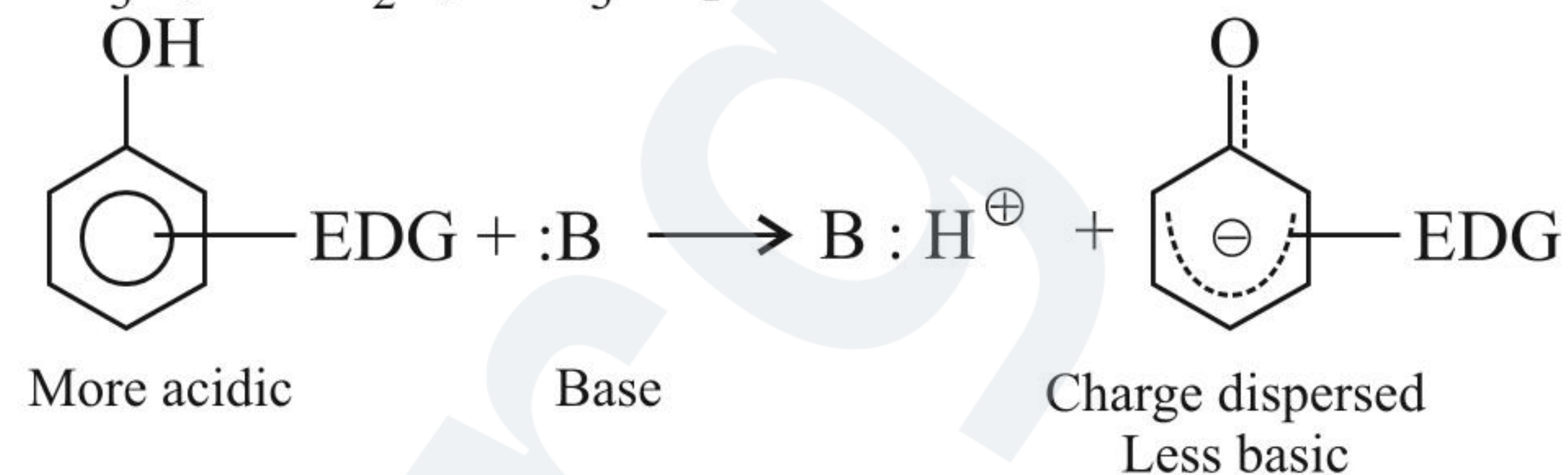
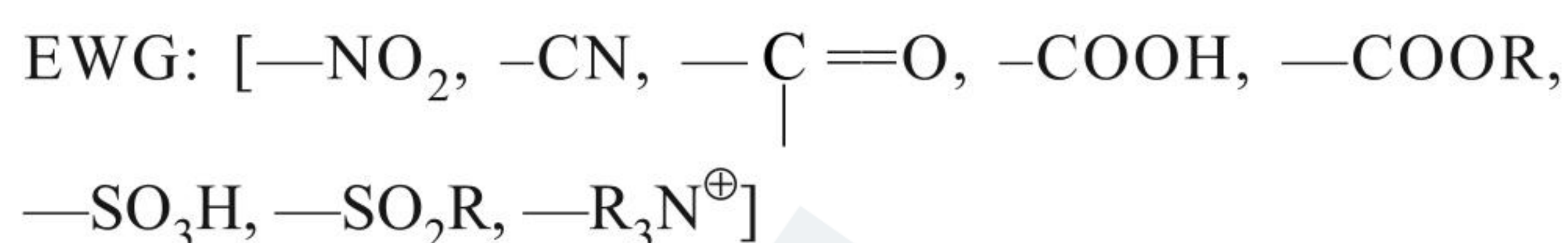
Alternatively: Both phenol and phenoxide ion are resonance-stabilised, whereas neither alcohols nor alkoxides are resonance-stabilised. Therefore, phenol is a stronger acid than alcohols.

Similarly, one can account for the weak acidic character of cyclohexanol than phenol. Neither cyclohexanol nor cyclohexanol anion are resonance-stabilised.

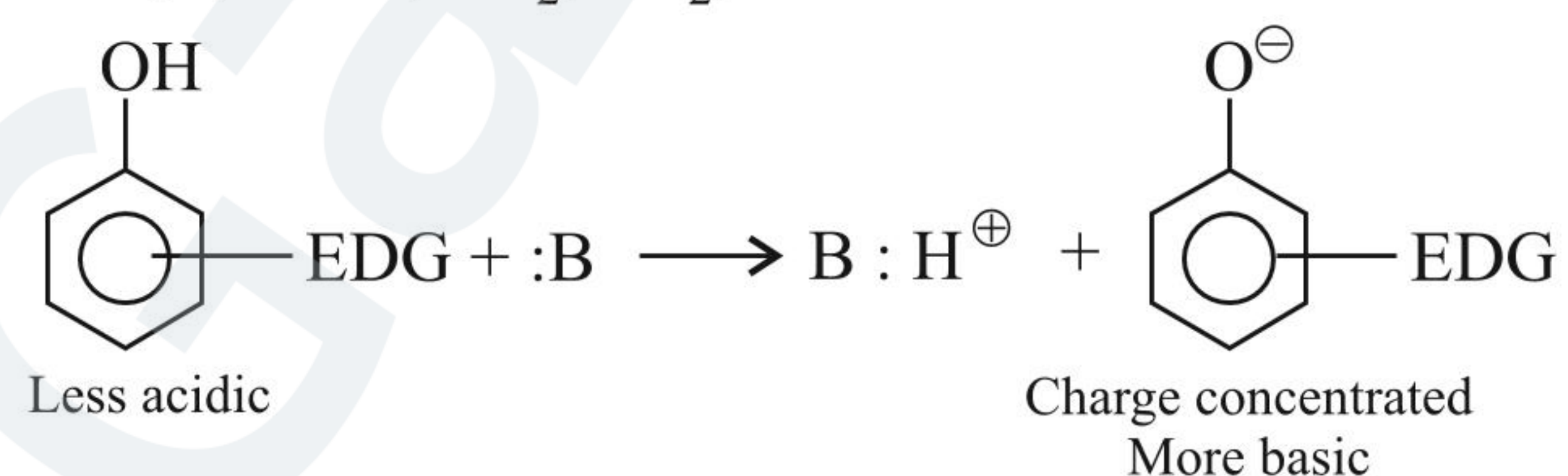


c. **Effect of electron-donating and electron withdrawing substituent on the acidity of phenols:**

i. e^- -withdrawing substituents disperse negative charges, making ArO^- a weaker base and the phenol a stronger acid.

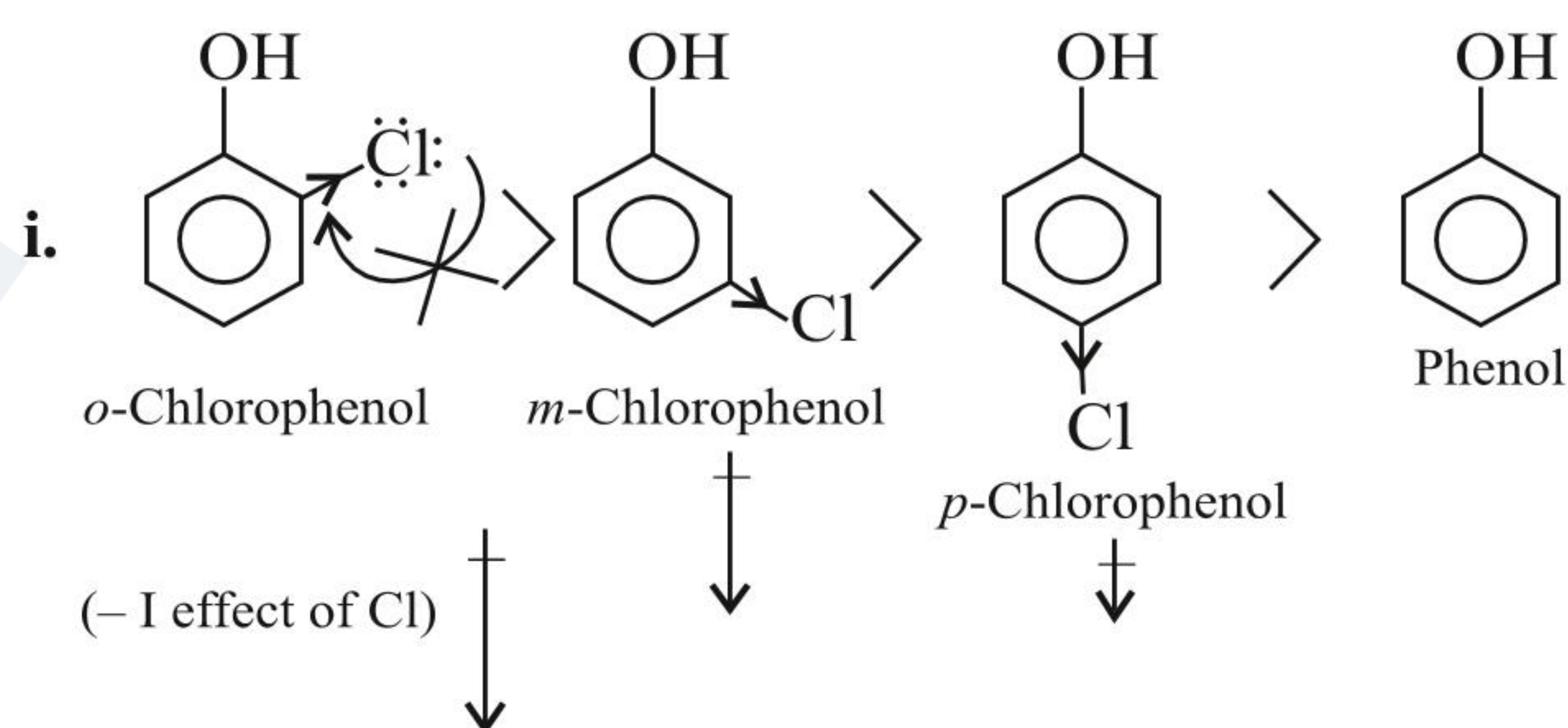


ii. e^- -donating substituents concentrate negative charges making ArO^- a stronger base and the phenol a weaker acid.



d. **Acidic character of substituted phenols:**

Decreasing acid strength of the following:

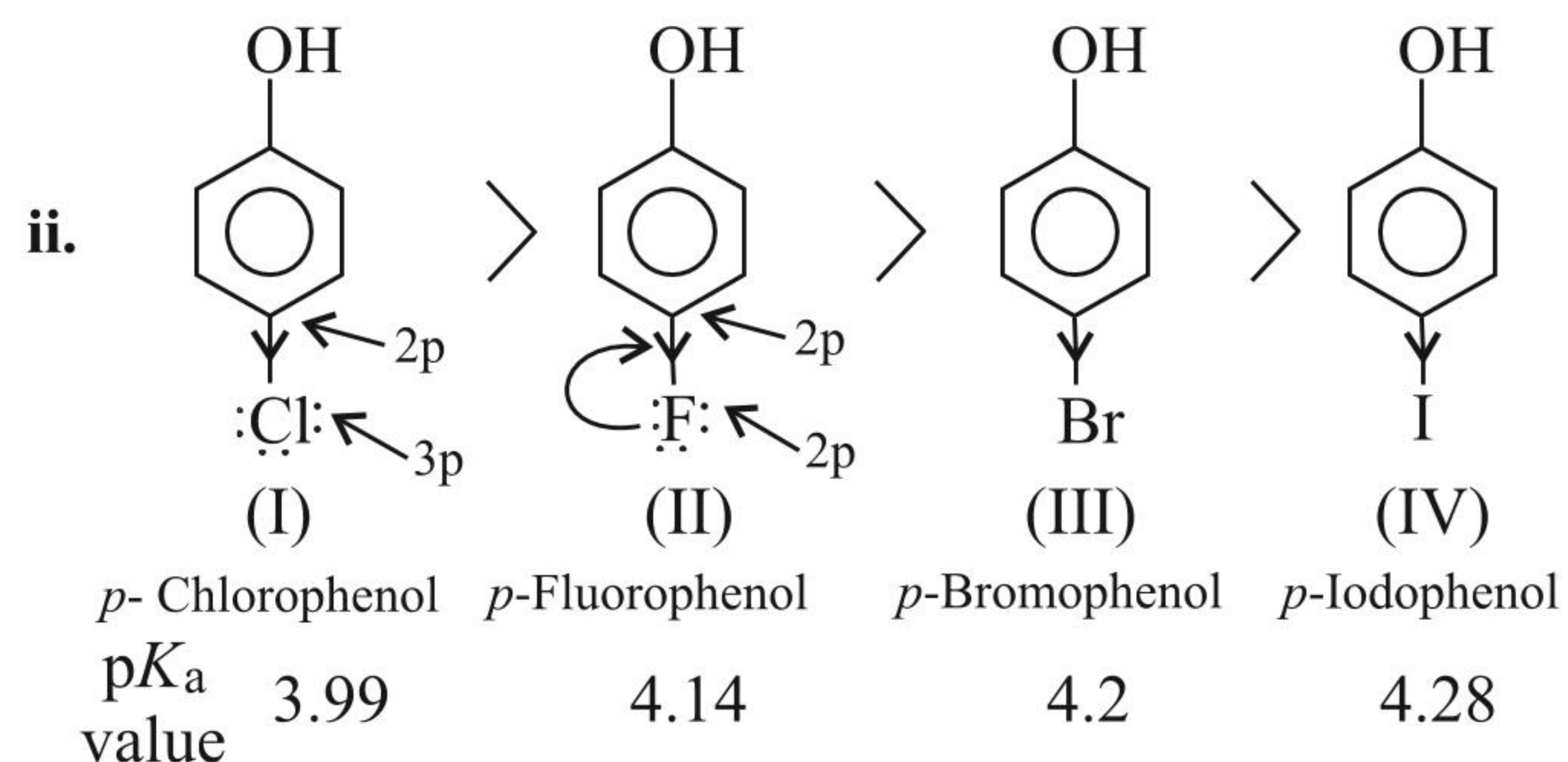


(-I effect of Cl or Br or I at $o- > m- > p-$)

In case of Cl, Br, and I, resonance effect due to LP of e^- 's on halogens does not operate (or weakly operate). In Cl, it is due to the ineffective overlap of $3p$ of Cl with $2p$ of C of benzene ring [i.e., $3p(\text{Cl})-2p(\text{C})$ overlap]. In Br and I, it is because of the ineffective overlap of $[4p(\text{Br})-2p(\text{C})]$ and $[5p(\text{I})-2p(\text{C})]$, respectively.

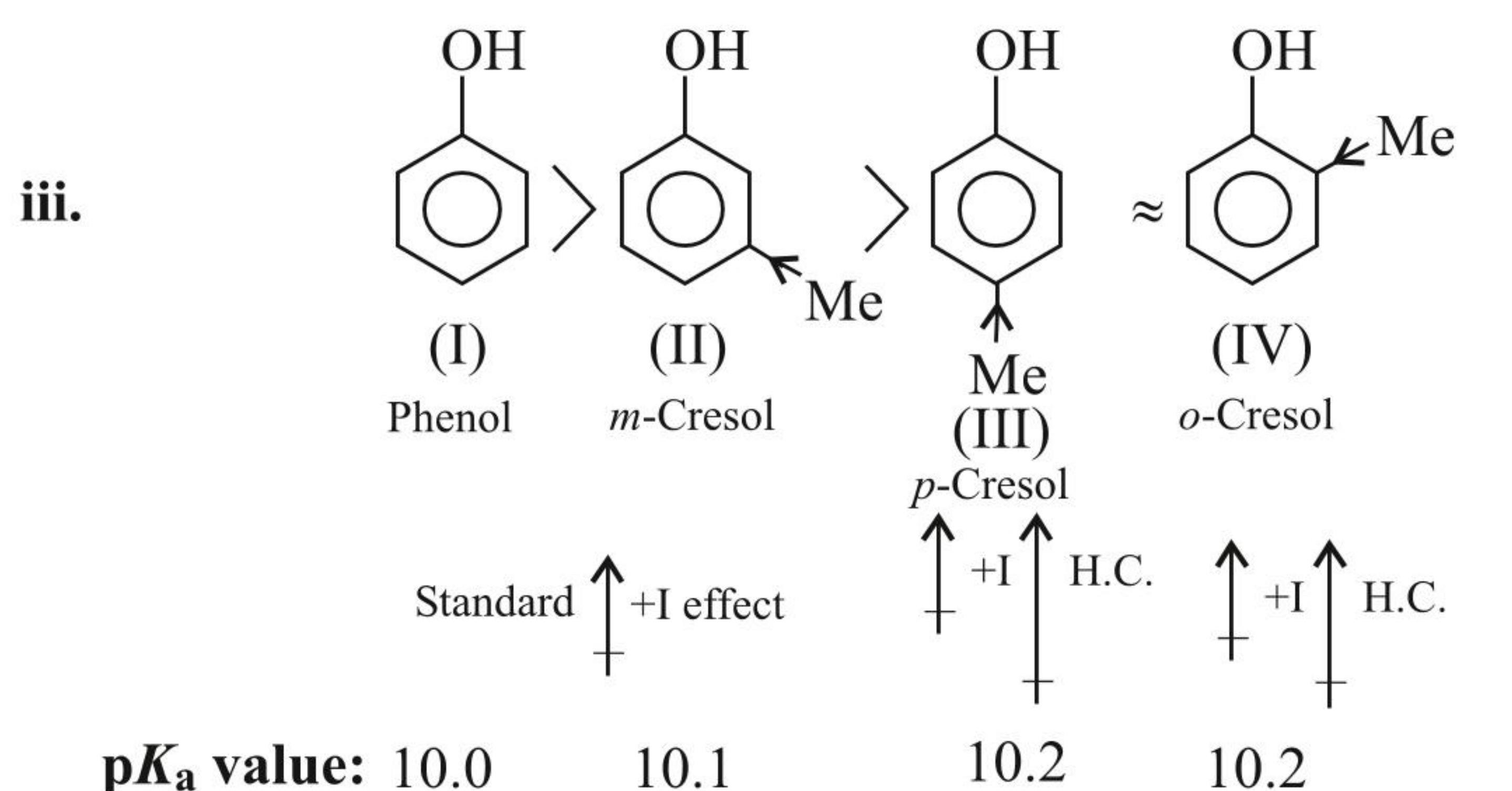
But in F, both -I and +R are operative, because in F there is effective overlap of $2p(\text{F})-2p(\text{C})$ of benzene ring.

In general, to decide the acidic character of substituted aryl halide, only -I effect is considered. In other words, one can conclude that -I effect of halogens (except F) is more predominant than +R effect.



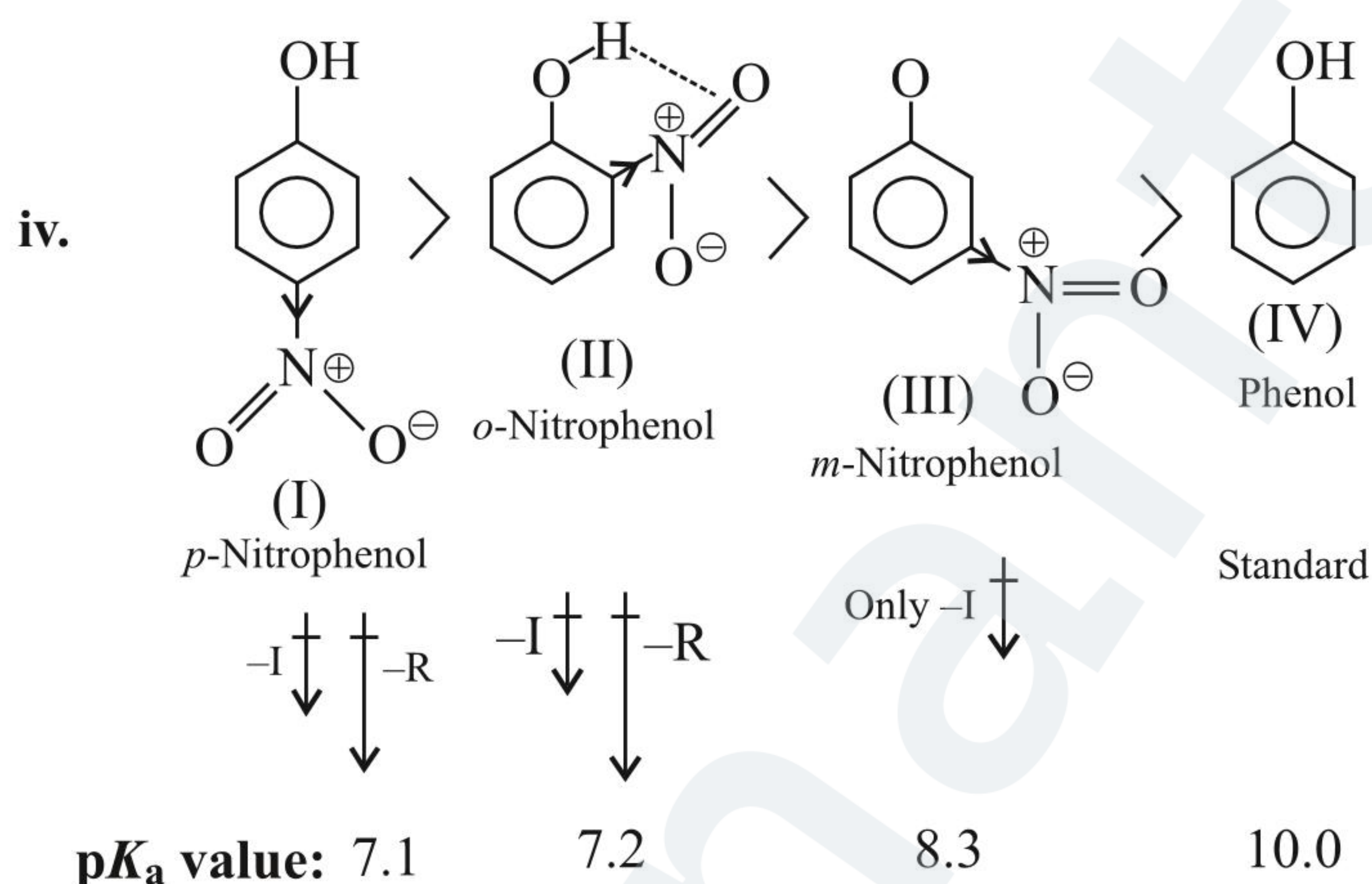
(-I effect of $F > Cl > Br > I$)

In (I), (III), and (IV), only -I effect is predominant, but in (II) both -I and +R are predominant because of the effective overlap of $2p(F)-2p(C)$. Net \bar{e} -withdrawing effect in (II) is less than (I) but greater than (III) and (IV).



[+I effect of (Me) group at $o > m > p$
Hyperconjugative effect (H.C.) of (Me-) group
only at *o*- and *p*-position and equal at both positions.
H.C. effect does not operate at *m*-position]

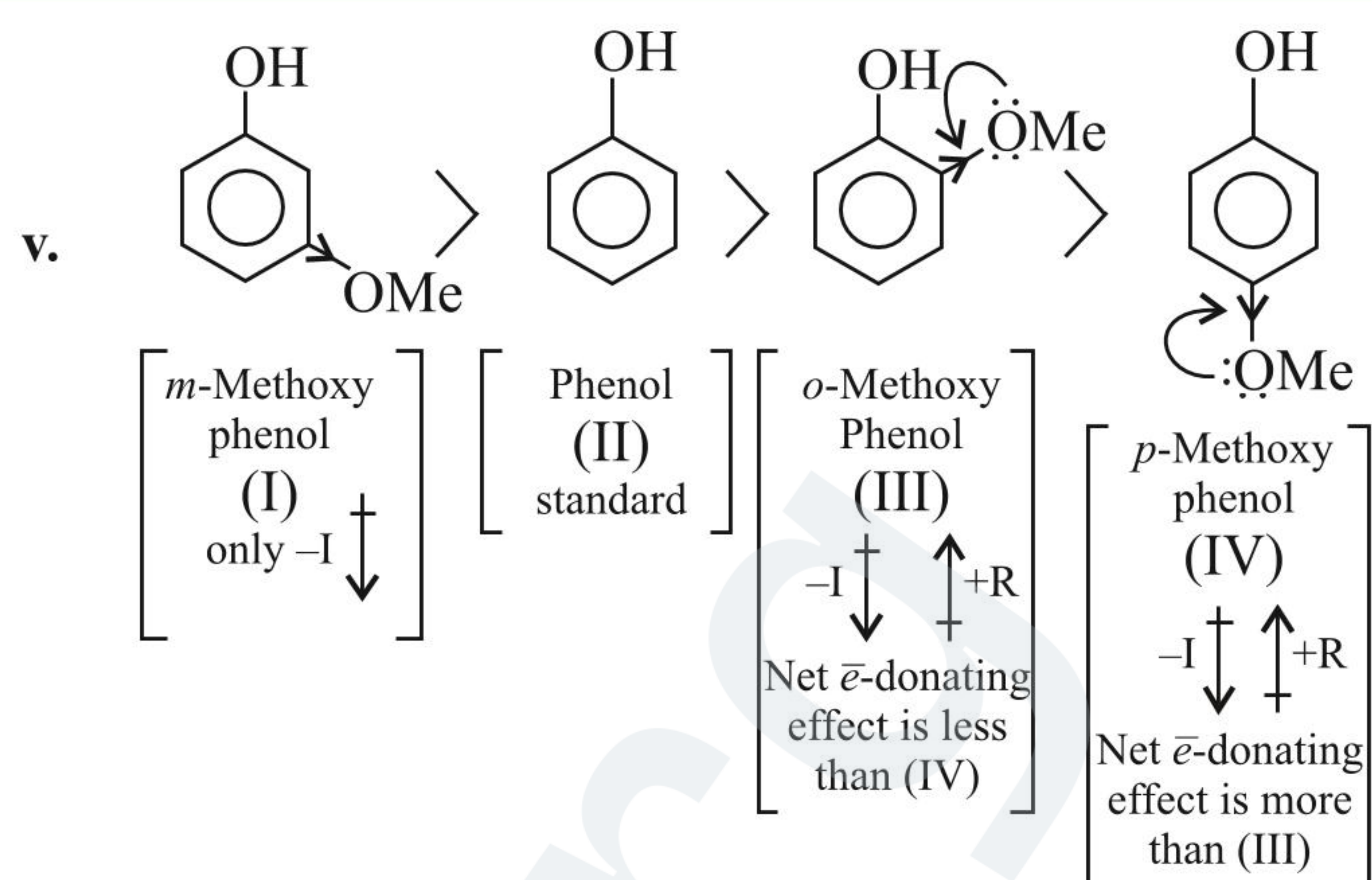
Net \bar{e} -donating power due to combined effect of +I and H.C. of (Me-) group in (III) is slightly less than (IV) (because +I at *ortho* > at *para*). So, (III) should be slightly more acidic than (IV). But pK_a value shows equal acidic strength of (III) and (IV). This suggests that difference in +I effect at *o*- and *p*-position is insignificant.



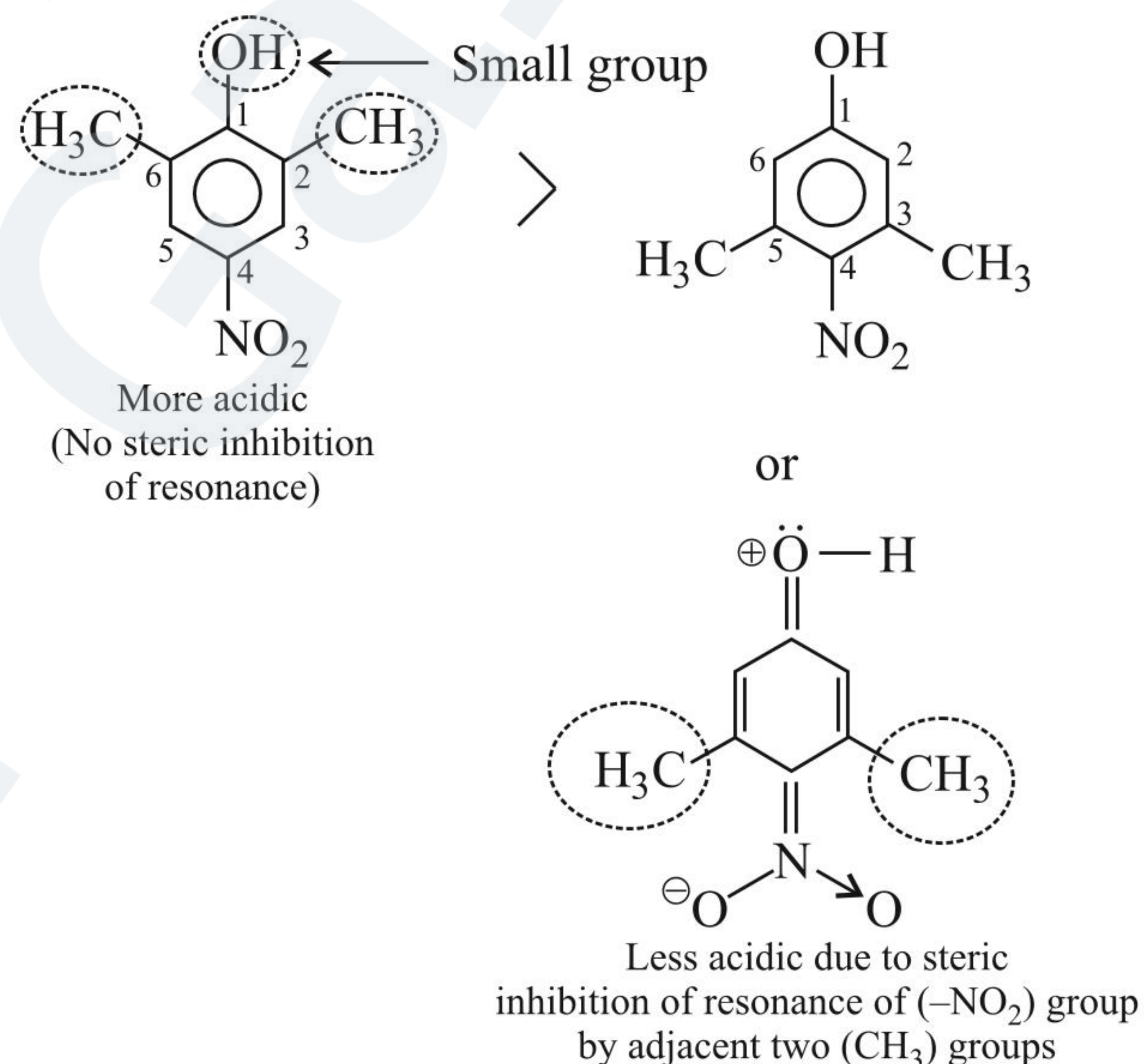
-I effect of ($-\text{NO}_2$) group at $o > m > p$.

-R effect of ($-\text{NO}_2$) group only at *o*- and *p*-position and equal at both positions.

So combined \bar{e} -withdrawing effect due to -I and -R is greater in (II) than in (I). So (II) should be more acidic than (I). But pK_a value shows that (I) is more acidic than (II). However, the intramolecular H-bond in (II) makes (II) less acidic than in (I), because some energy is required to break H-bonding. Further, (III) is more acidic than (IV) because of -I effect of ($-\text{NO}_2$) group at *m*-position.

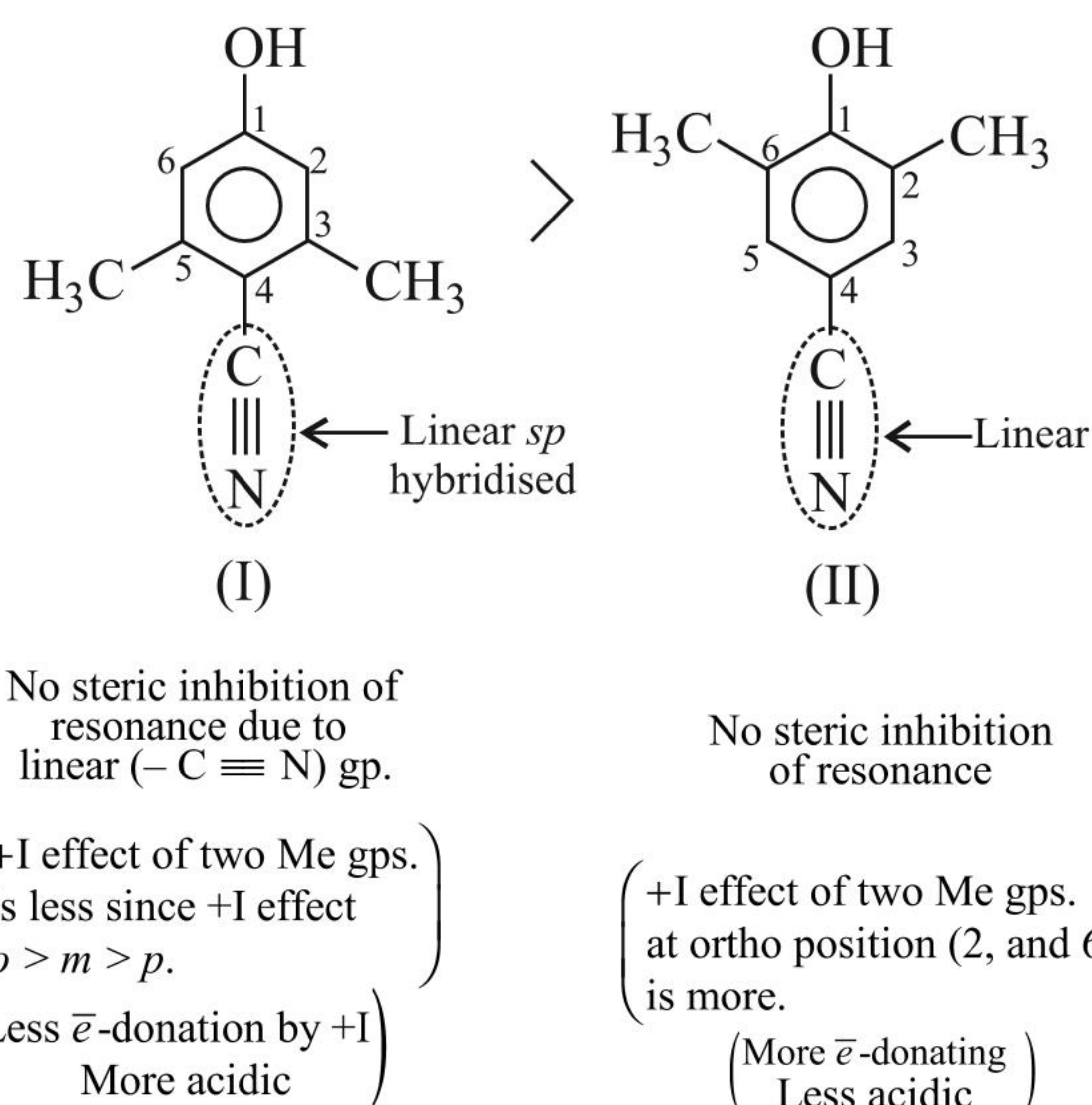


vi. 3,5-Dimethyl-4-nitrophenol is less acidic than the isomeric 2,6-dimethyl-4-nitrophenol.



The O atoms of ($-\text{NO}_2$) group are hindered from lying in the plane of aromatic ring by the presence of two ($-\text{CH}_3$) groups at the adjacent C atom. It causes a large inhibition to resonance and hence is less acidic.

vii. But 3,5-dimethyl-4-cyano phenol is more acidic than the isomeric 2,6-dimethyl-4-cyanophenol.



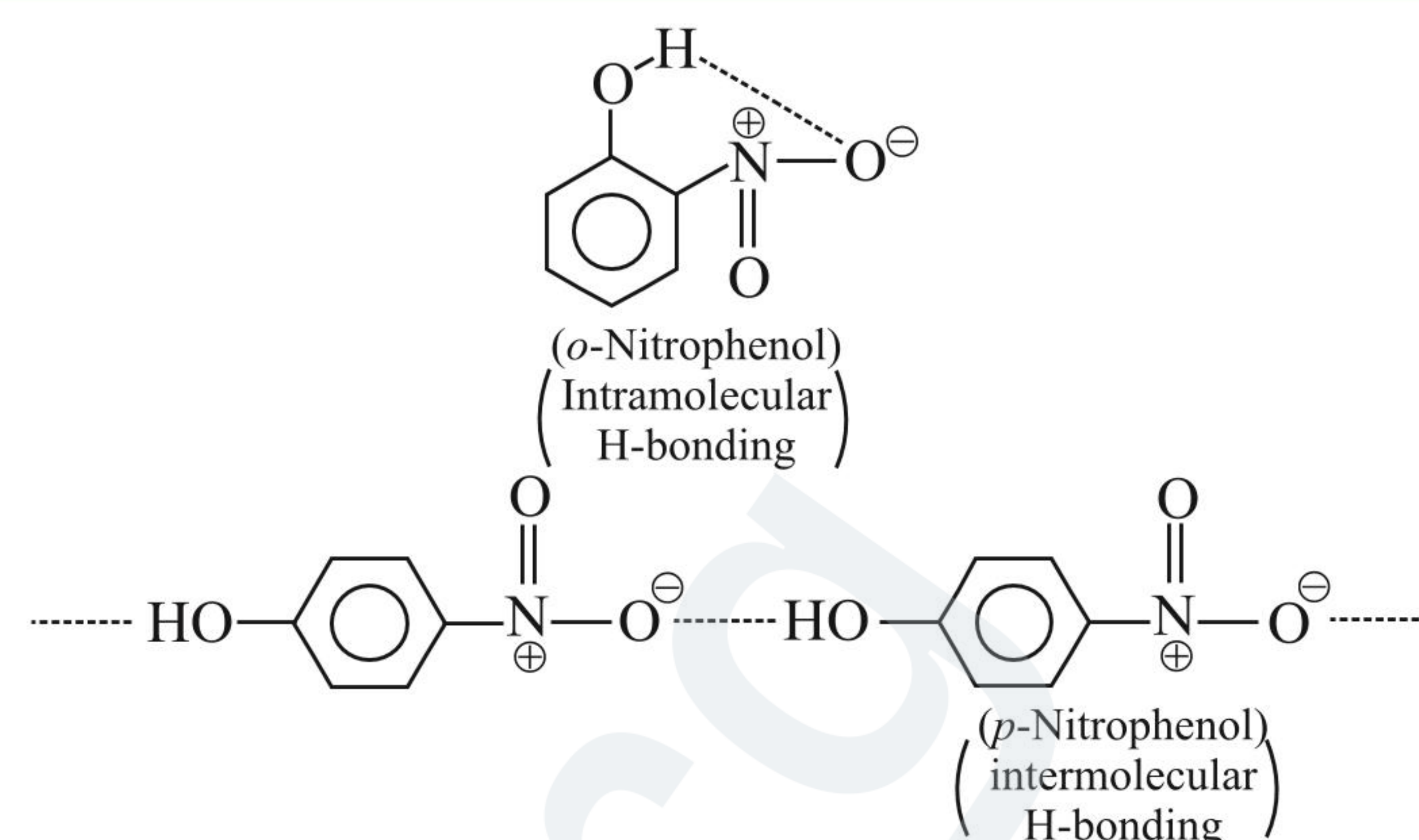
Note: There is no steric hindrance between (OH) group and two (Me) groups at 2, and 6 in both cases (vi) and (viii), since (—OH) group is small.

ILLUSTRATION 4.11

Arrange the following compounds in increasing order of their acid strength:

(I) Propan-1-ol, (II) 2, 4, 6-trinitrophenol, (III) 3-nitrophenol, (IV) 3, 5-dinitrophenol, (V) phenol, (VI) 4-methylphenol

Sol. I < VI < V < III < IV < II

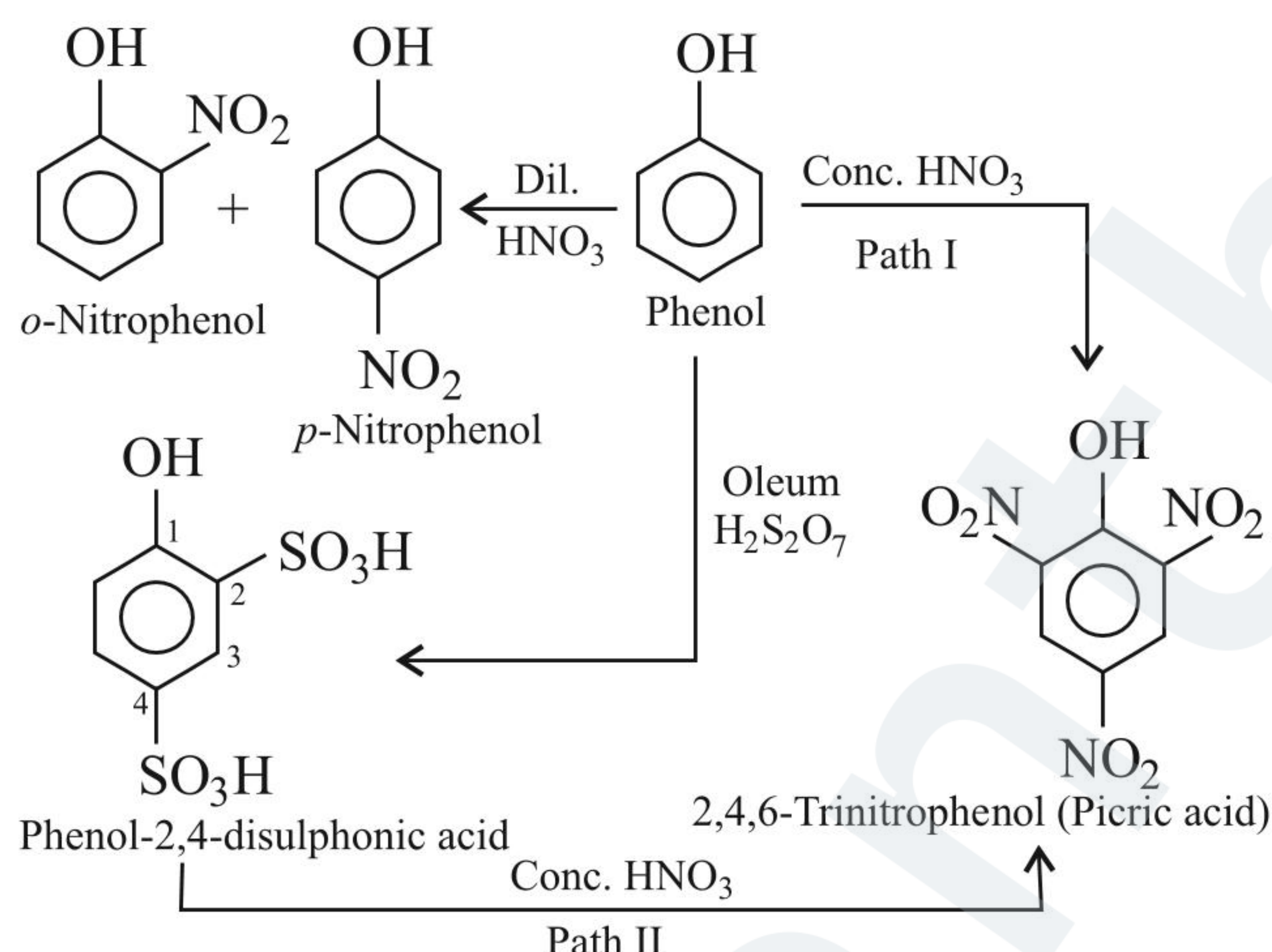


4.15 SOME REACTIONS OF PHENOLS

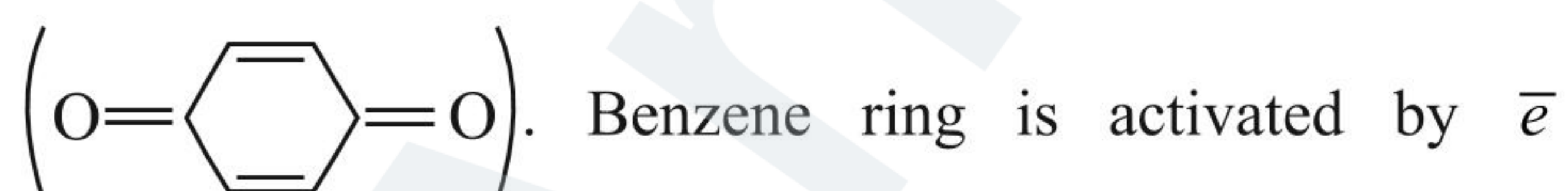
a. SE (substitution by electrophile) reaction:

For detailed discussion, see Chapter 3.

i. Nitration:



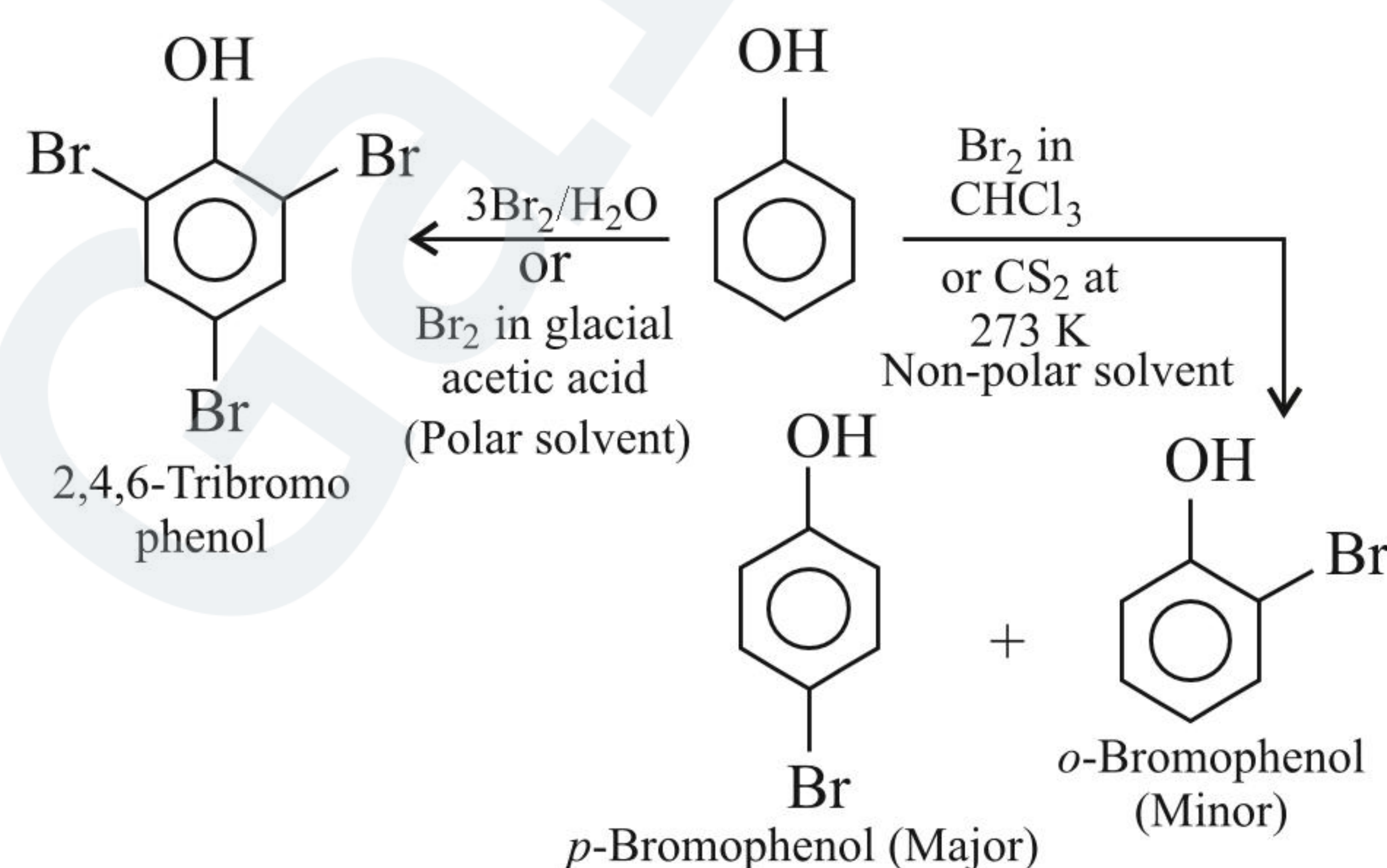
Better yield of picric acid is obtained by path II, since by path I some of the phenol is oxidised to *p*-benzoquinone



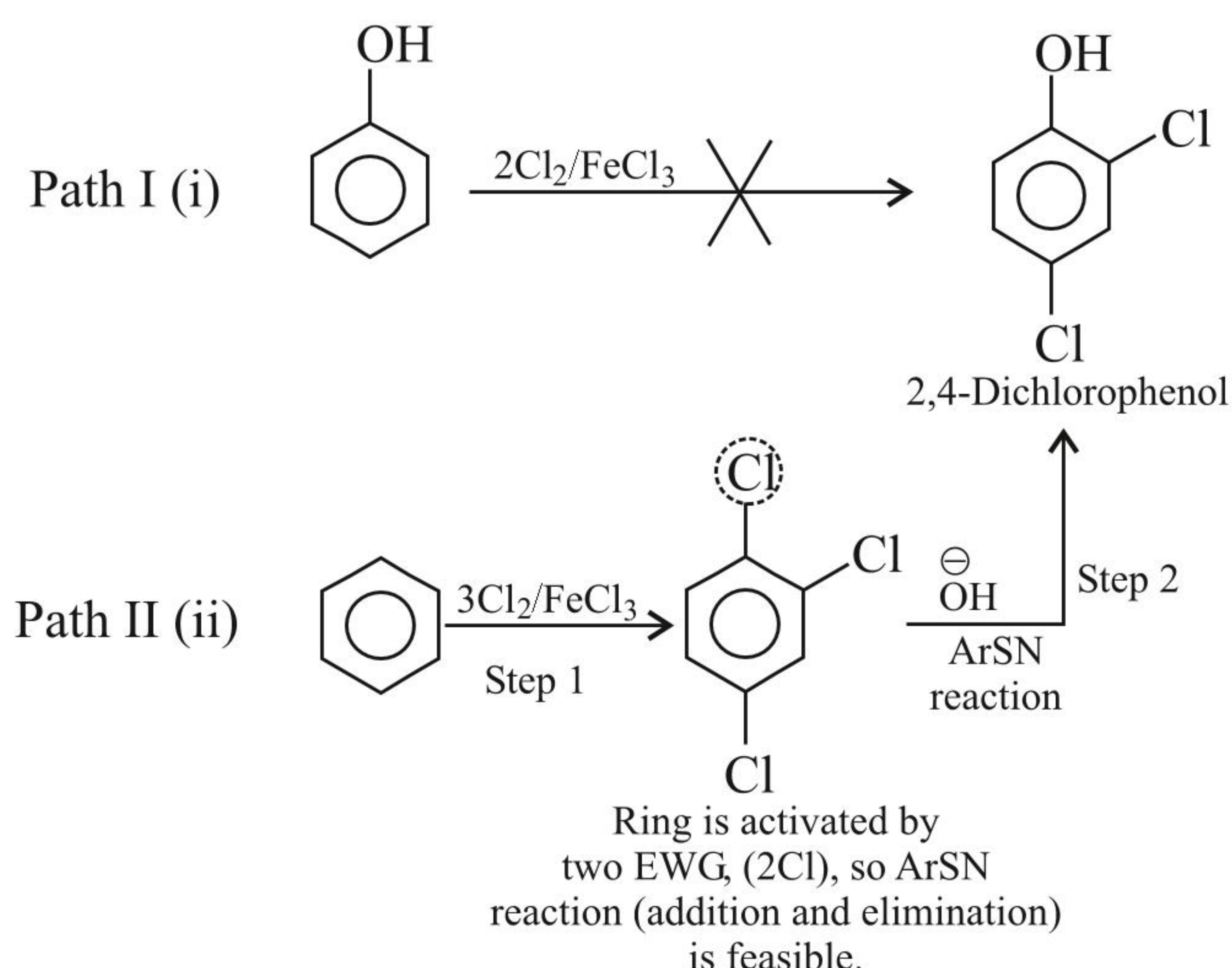
—donating +R effect of (—OH) groups and is oxidised to *p*-benzoquinone. But in path II, due to \bar{e} -withdrawing —I and —R effects of two (—SO₃H) groups, benzene ring is deactivated and is not oxidised and therefore picric acid is obtained in almost 100% yield. The (—SO₃H) group is substituted by (—NO₂) group by ipso substitution.

The *o*- and *p*-nitrophenol are separated by steam distillation; *o*-isomer is steam volatile due to intramolecular H-bonding, while *p*-isomer is less volatile due to intermolecular H-bonding which causes association of molecules.

ii. Halogenation



iii. Phenol cannot be chlorinated because the ring is reactive (due to strong EDG) and is susceptible to oxidation by Cl₂ to benzoquinone.

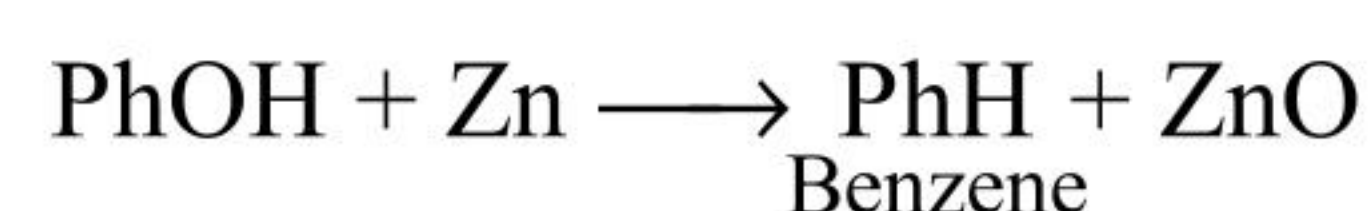


Therefore, preparation of 2,4-dichlorophenol from phenol is not feasible by path I, but the same can be prepared by path II.

In step 2 of path II, the displaced Cl is *ortho* to one other Cl and *para* to the other and is activated by both. Each of the Cl atoms is *meta* to at least one deactivating Cl.

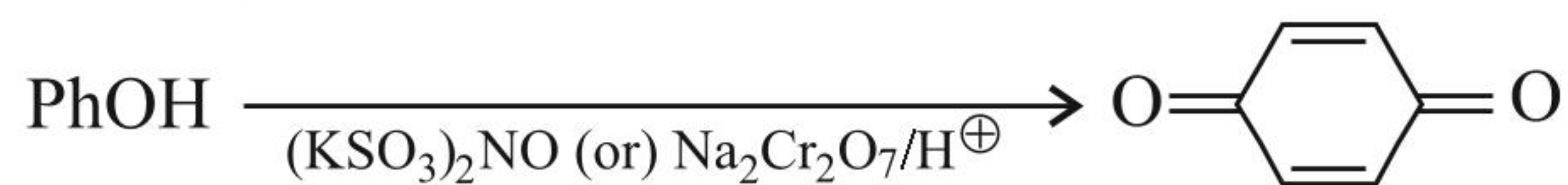
b. Reaction of phenol with Zinc dust:

Phenol is converted to benzene on heating with zinc dust.

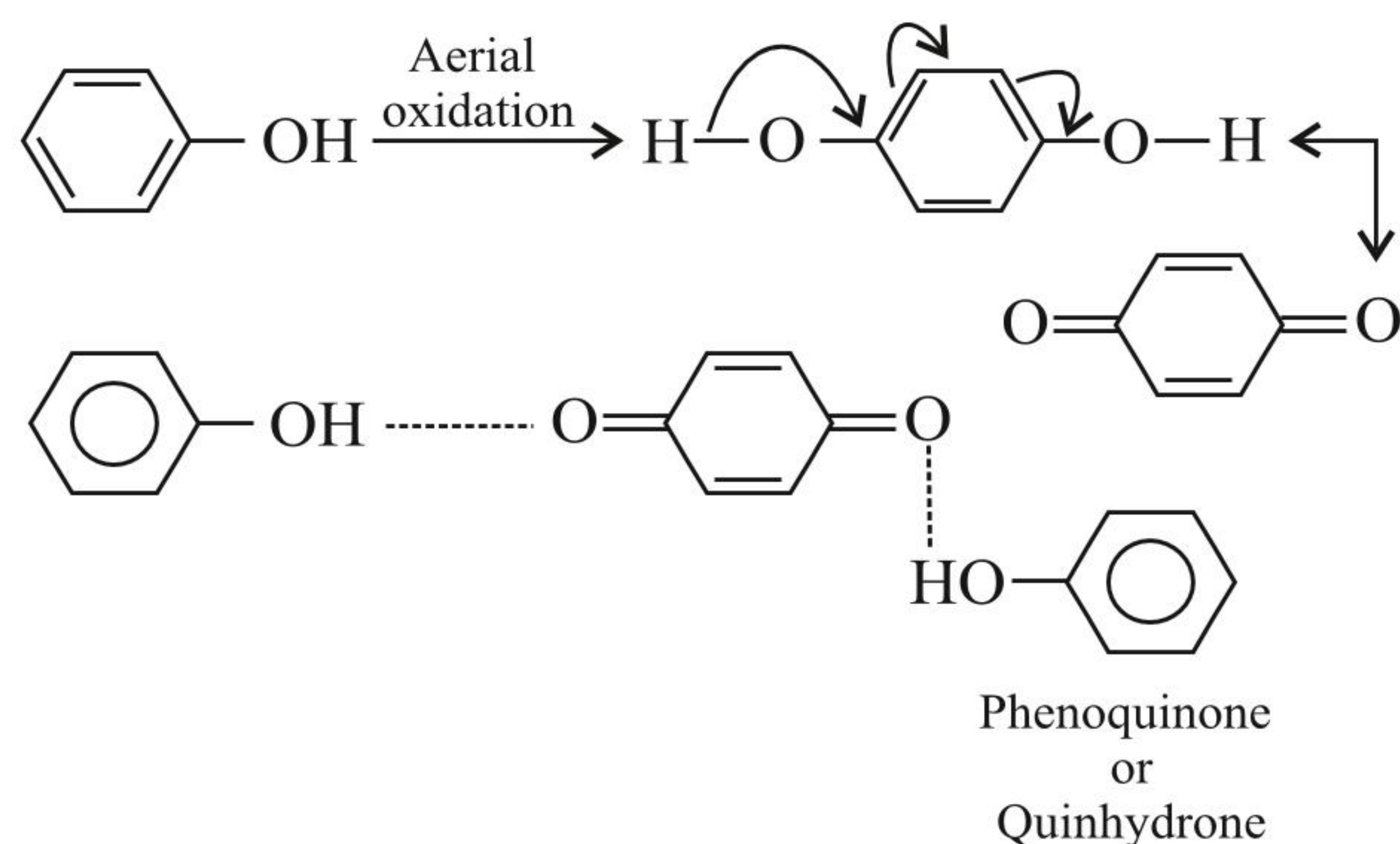


c. Acetylation, benzylation, and tosylation of alcohols and phenols: For detailed discussion, see Chapter 3.

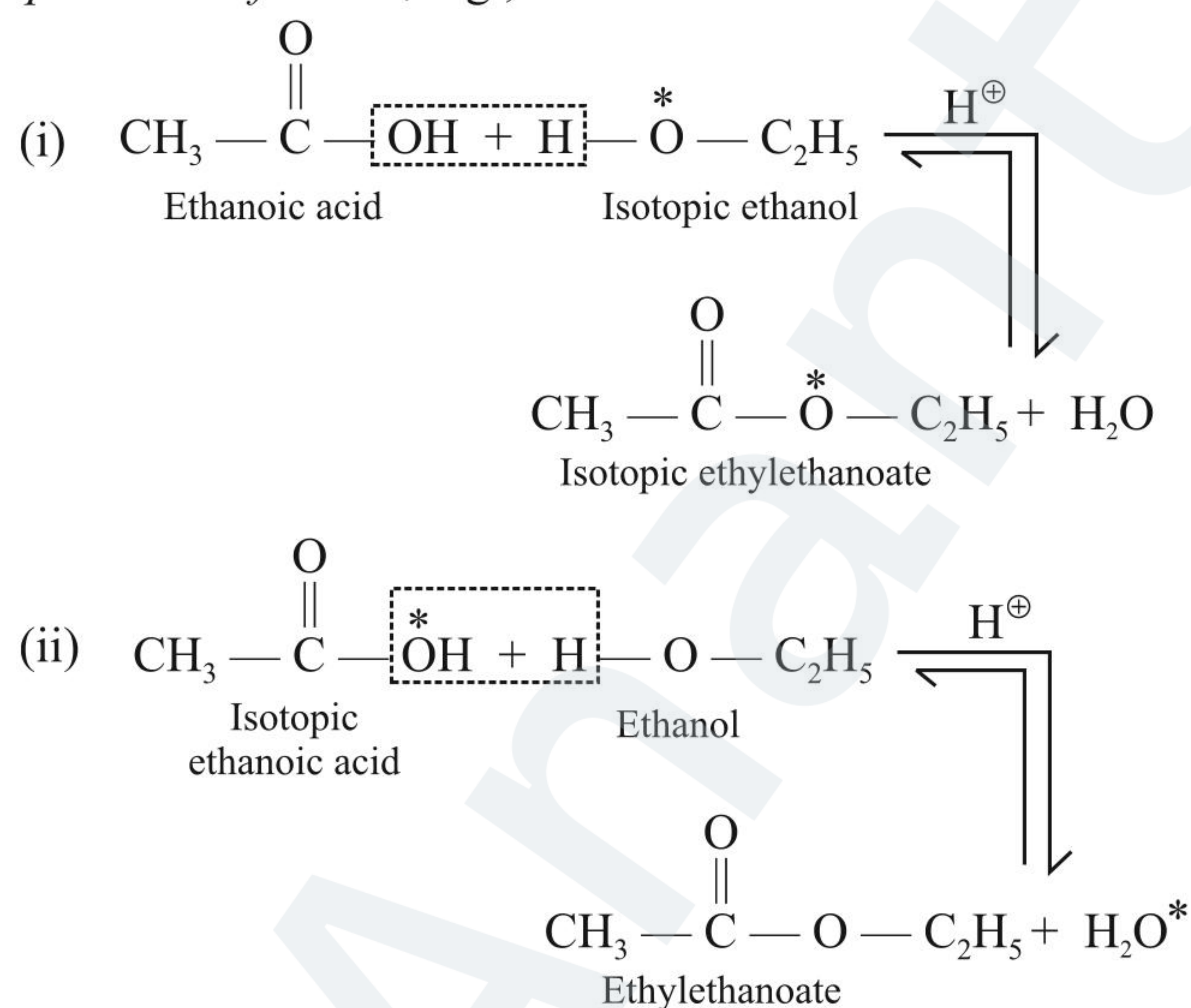
- d. **Oxidation:** Phenol with chromic acid or with Fremy's salt $(\text{KSO}_3)_2\text{NO}$ is oxidised to coloured *p*-benzoquinone.



- e. Phenol turns pink on exposure to air and light due to slow oxidation. Complex mixture of products is formed on oxidation by air or other oxidising agents. One of the oxidation products in air is quinone which forms a brilliant red addition product with phenol known as phenoquinone, in which two phenol molecules are joined to one molecule of quinone through H-bonds.



- f. **Esterification:** Carboxylic acids are esterified with alcohols and phenols in the presence of HCl(g) or conc. H_2SO_4 as catalyst. If HCl(g) is used as catalyst it is called *Fischer speier esterification*, e.g.,



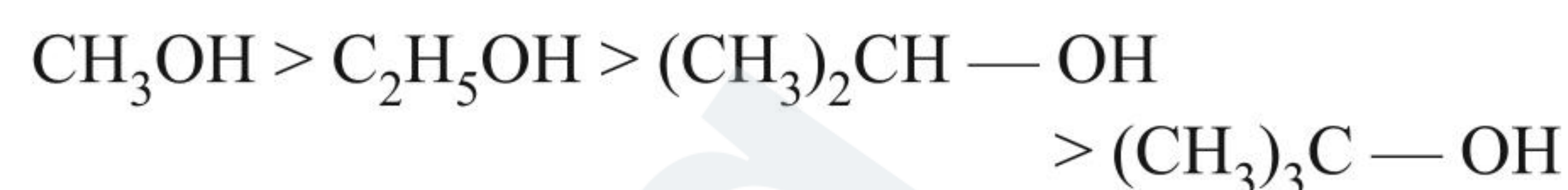
The above two isotopic experiments suggest that the ester is formed by the removal of $(-\text{OH})$ group from acid and H-atom from alcohol.

- (iii) The following two observations suggest that esterification is a reversible reaction. According to Le-chatelier's principle, the equilibrium is shifted to forward direction if H_2O is removed by azeotropic distillation with benzene and if the esterification is carried out in excess of alcohol.

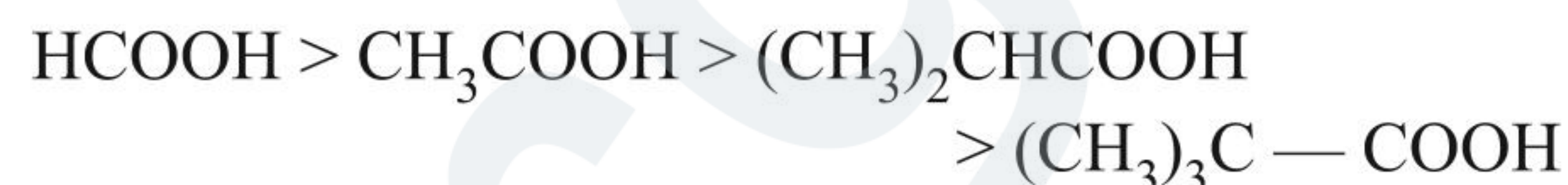
Reactivity order of esterification:

- i. The reactivity of esterification decreases with the increase in number of C-atom in both alcohol and carboxylic acid.

For example: $1^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 3^\circ \text{ alcohol}$

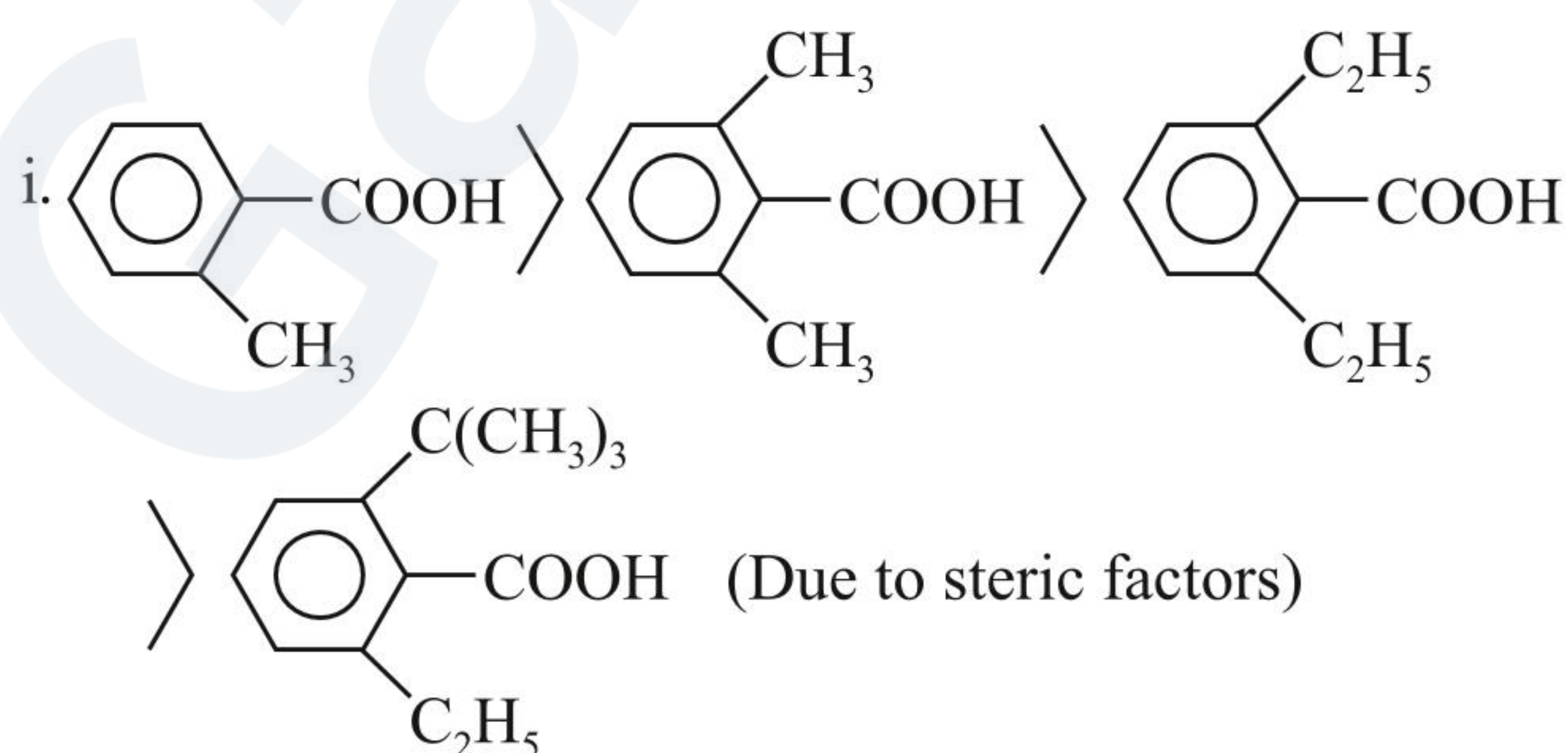


and

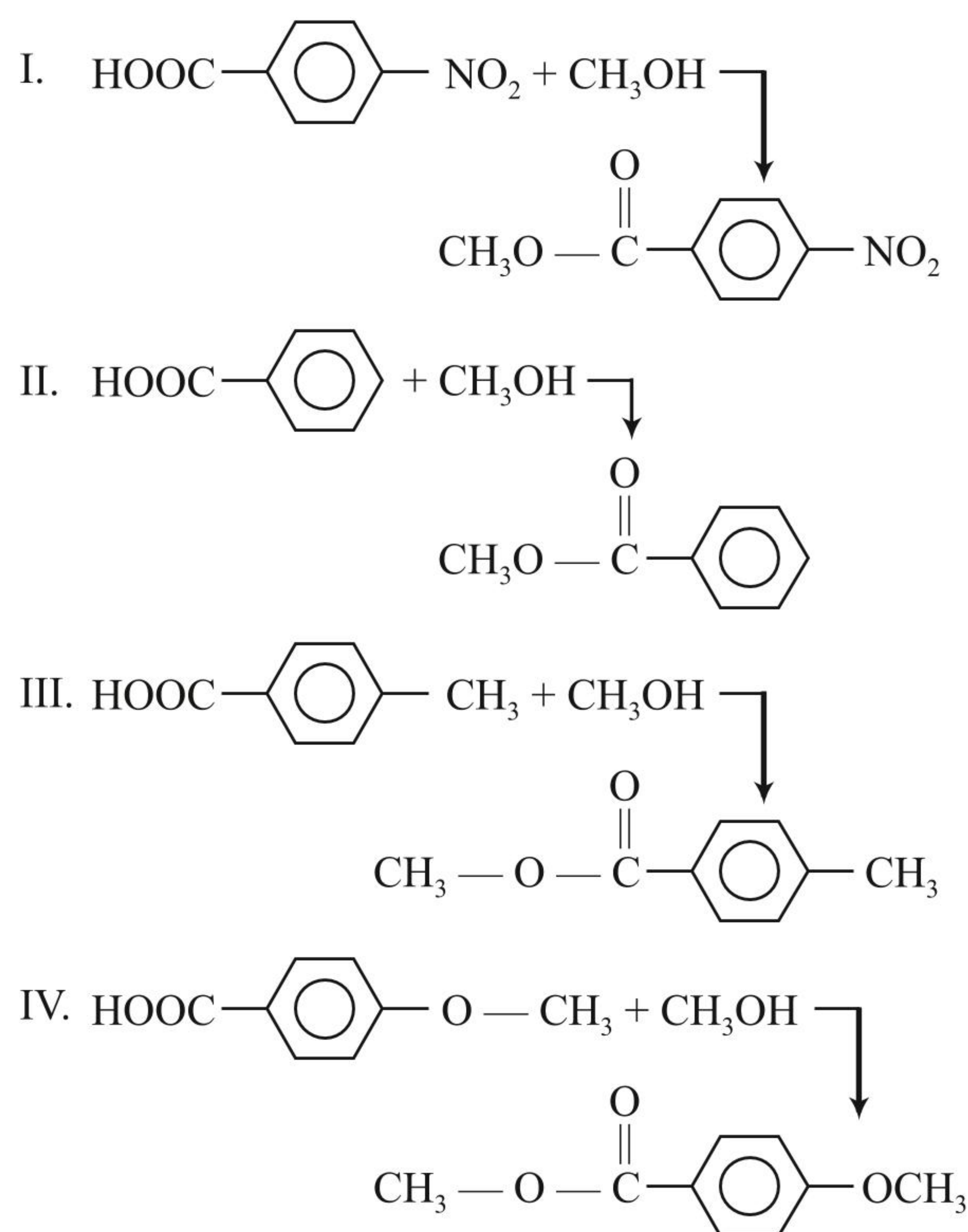


- ii. In case of aromatic acids, esterification decreases with increase in the number of alkyl groups at *o*-position.

For example: Esterification reactivity of the following acids with CH_3OH



- ii. Ease of esterification of aromatic acid. More EWG group at *o*, and *p*-position in acids favours esterification. For example:

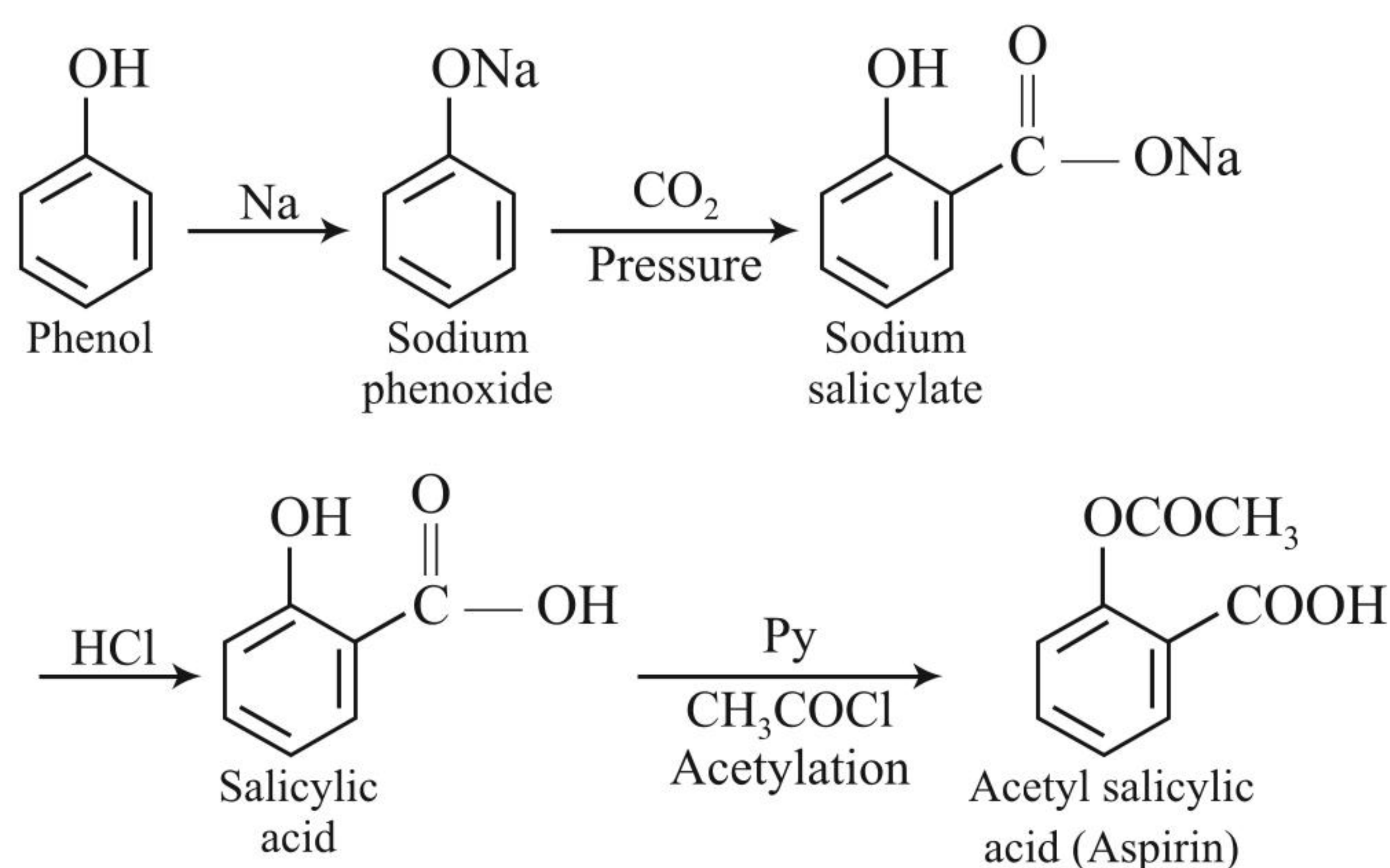


Ease of esterification: I > II > III > IV

- I. $[(-\text{NO}_2), -\text{M} \text{ and } -\text{I (or } -\text{R)}] \text{ at } p\text{-position} >$
 II. $[(\text{Ph}), -\text{I} \text{ and } +\text{M(standard)} >$

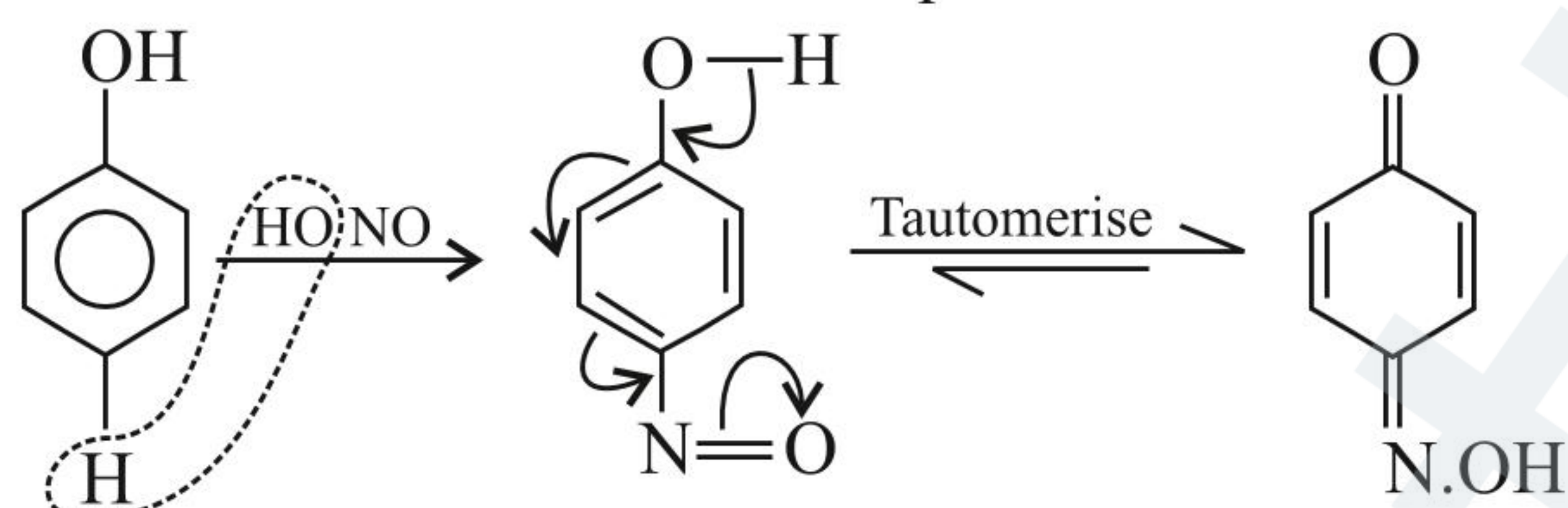
III. $[\text{CH}_3]$, (+I and H.C)]>IV. $[-\text{OCH}_3, -\text{I} \text{ and } +\text{M}, \text{ net more EDG than III}]$

- g. Aspirin synthesis:** Aspirin can be synthesised from the phenol as

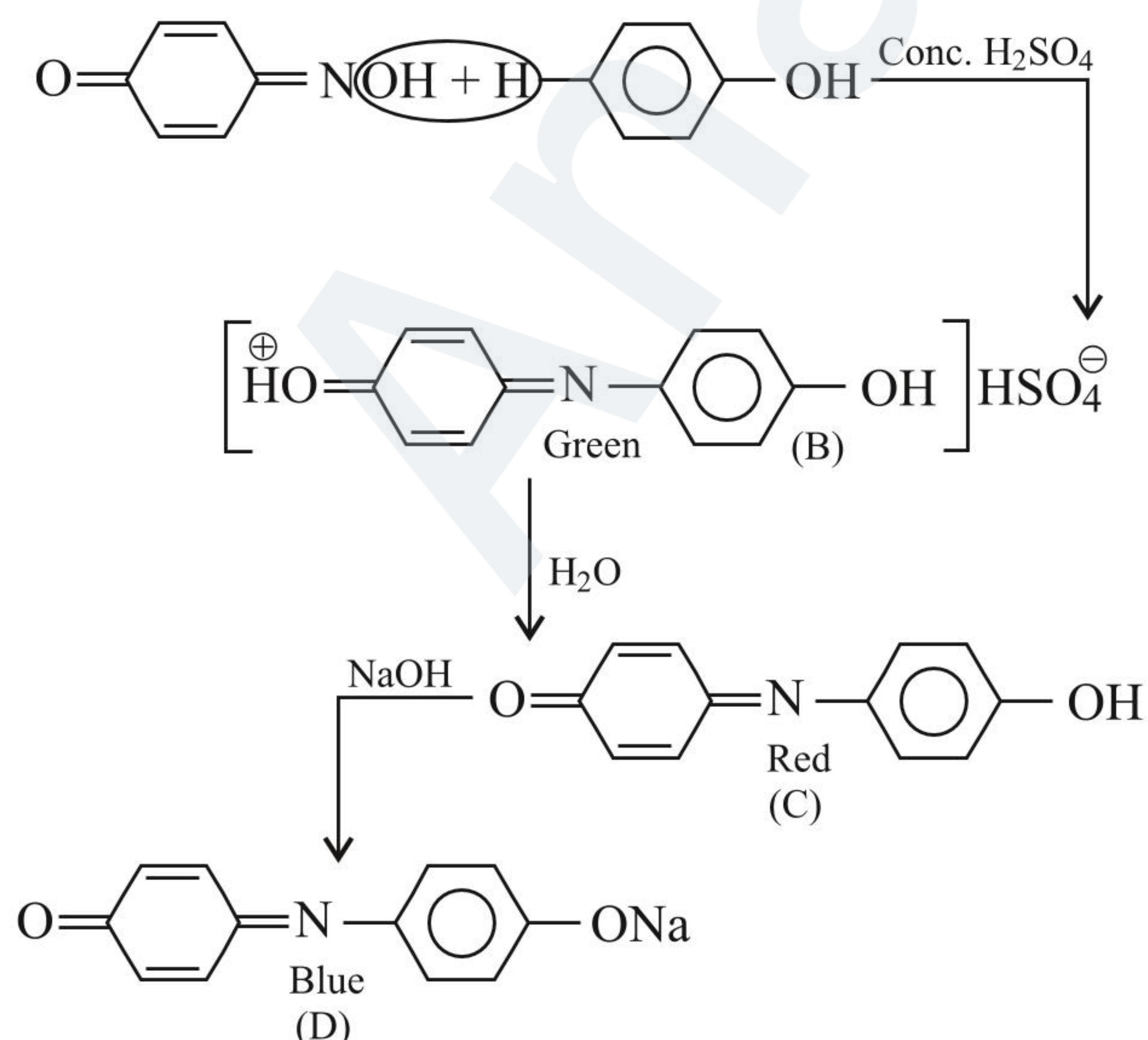


4.16 REACTION OF PHENOL WITH HNO_2 OR $(\text{NaNO}_2 + \text{HCl})$ AT $0-5^\circ\text{C}$

Phenol reacts with (HONO) to give *p*-nitrosophenol which is tautomeric with the monoxime of quinone.

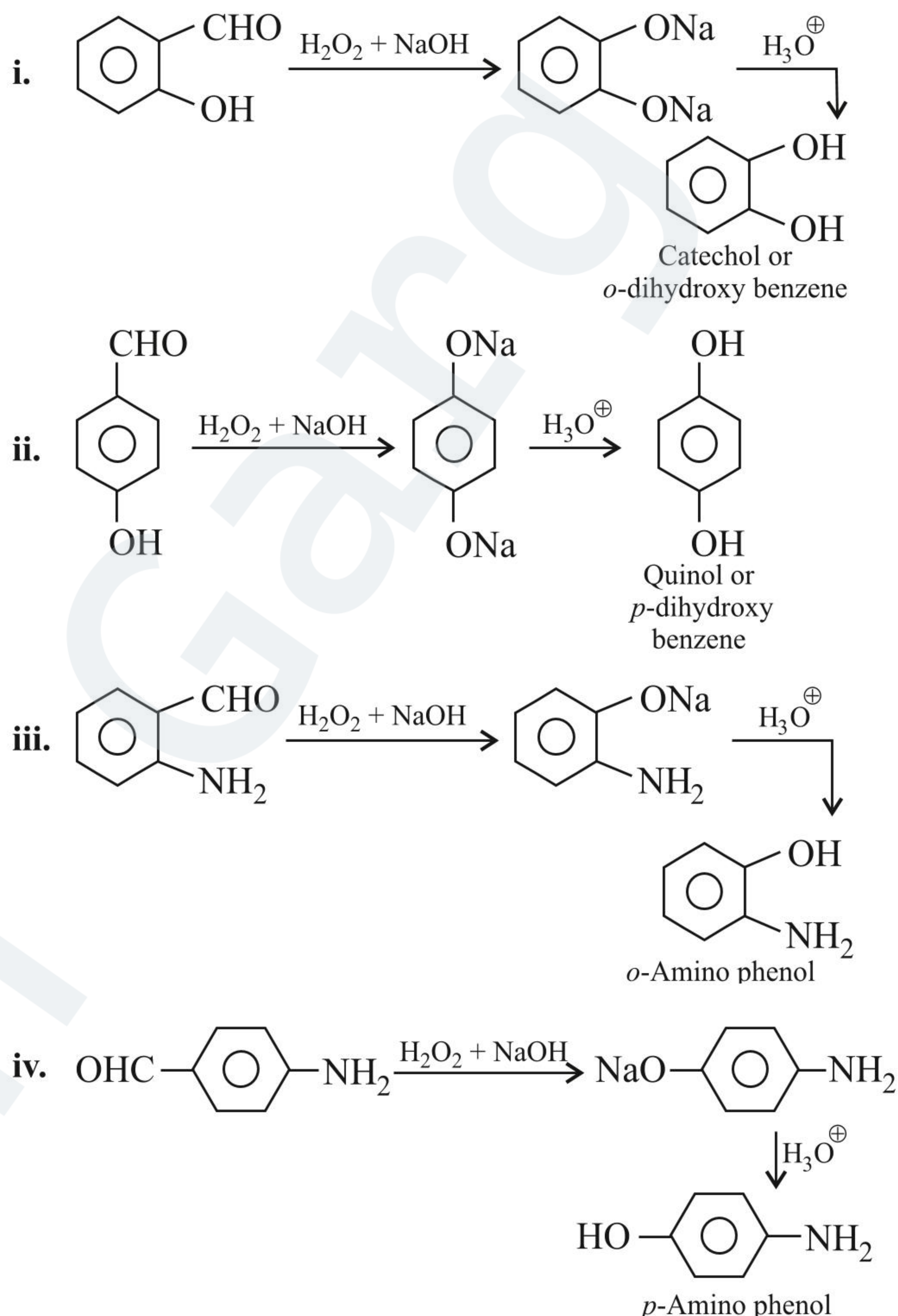


In the presence of conc. H_2SO_4 , the monoxime condenses with phenol to give blue-green solution of indophenol mono-sulphate which on dilution gives indophenol (red). With NaOH , sodium salt of indophenol (deep blue) is produced. This is **Libermann's nitroso reaction**.



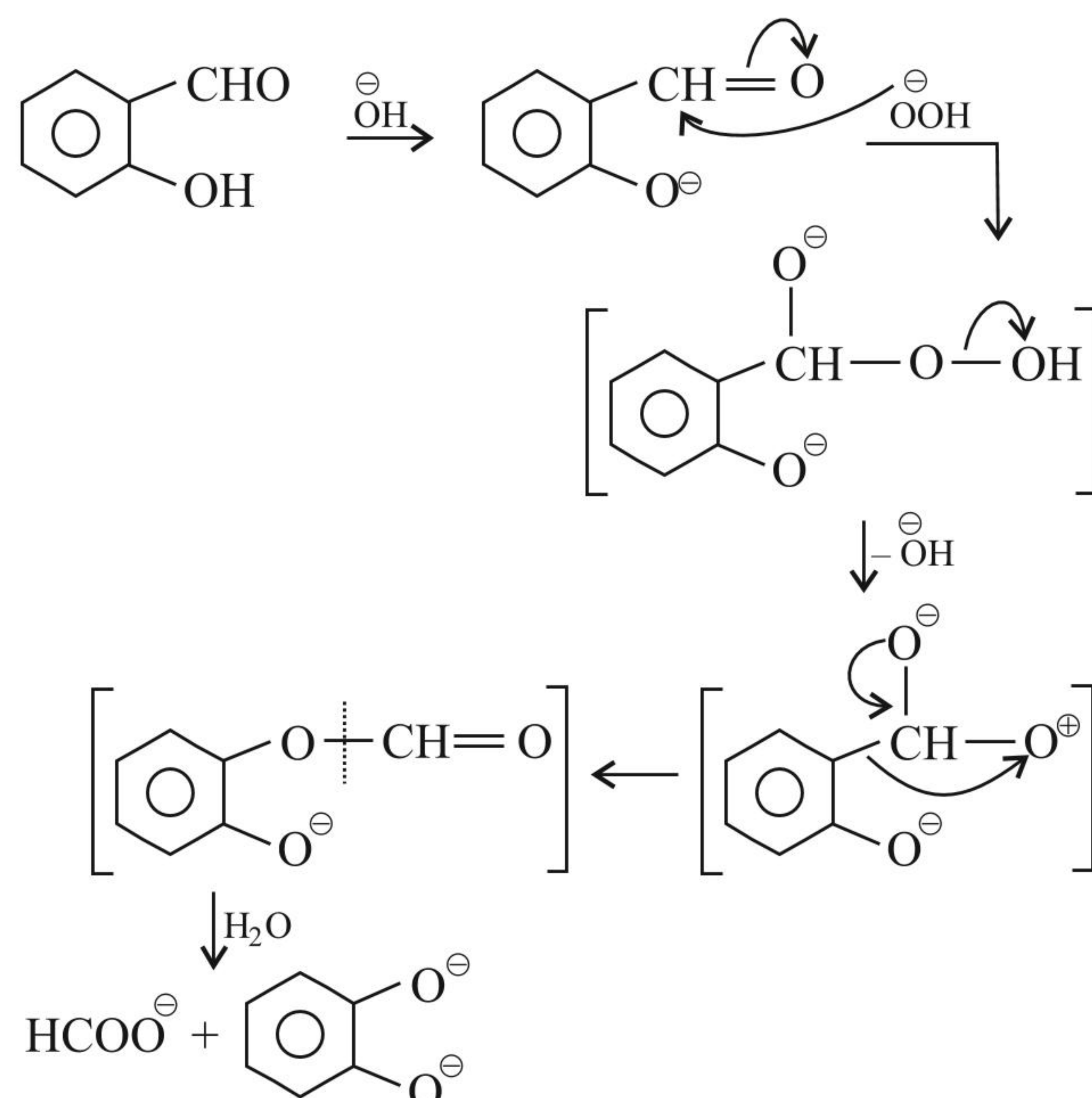
4.17 DAKIN REACTION

This reaction is characteristic of *o*- and *p*-hydroxy aldehyde or *o*- and *p*-amino aldehyde with alkaline H_2O_2 , followed by hydrolysis to give *o*- or *p*-dihydroxy benzene or *o*- or *p*-aminophenol, e.g.,



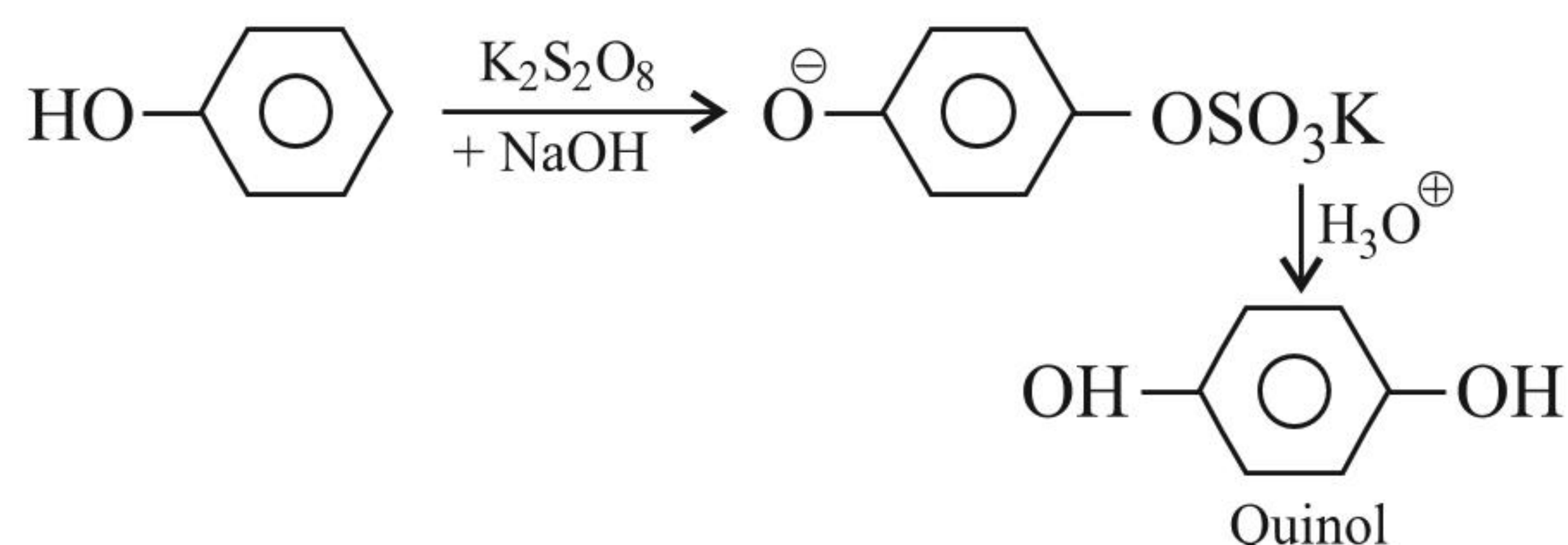
4.17.1 MECHANISM

It involves 1,2-shift.

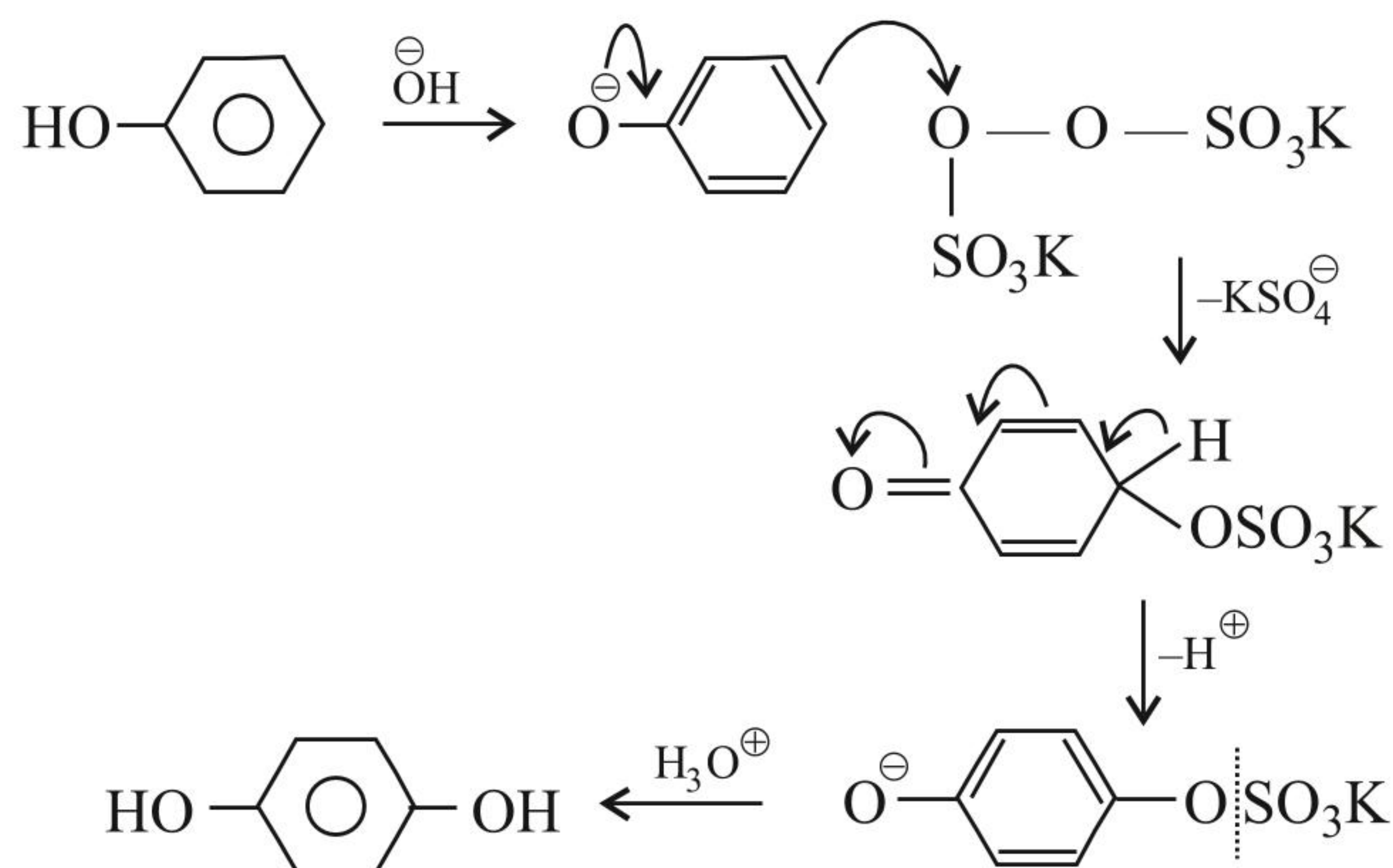


4.18 ELBS PERSULPHATE OXIDATION

In this reaction, monohydric phenols are oxidised to dihydric phenols by alkaline potassium persulphate ($K_2S_2O_8$). Hydroxylation normally occurs at *p*-position, but if this is blocked, then in the *o*-position, e.g.,

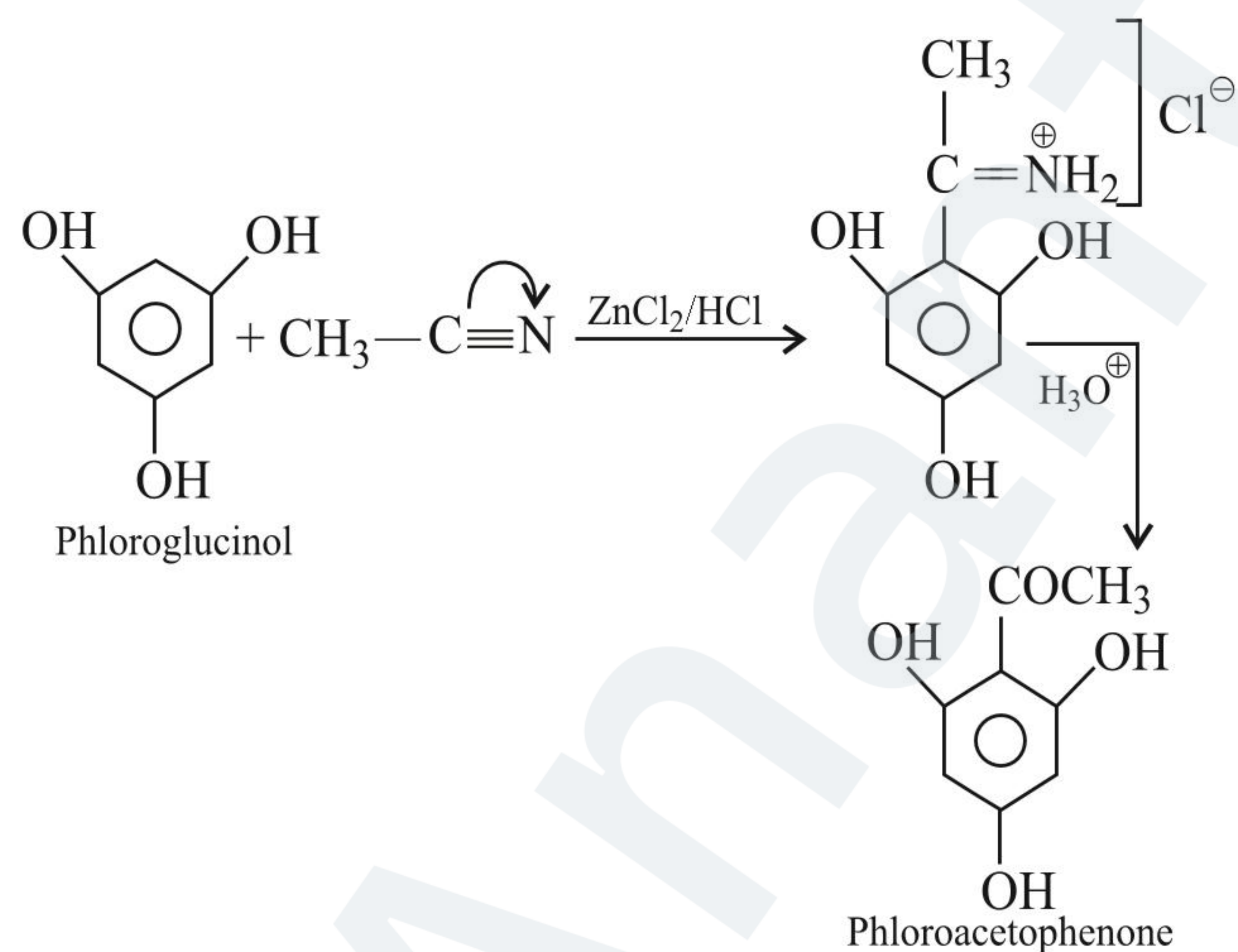


4.18.1 MECHANISM



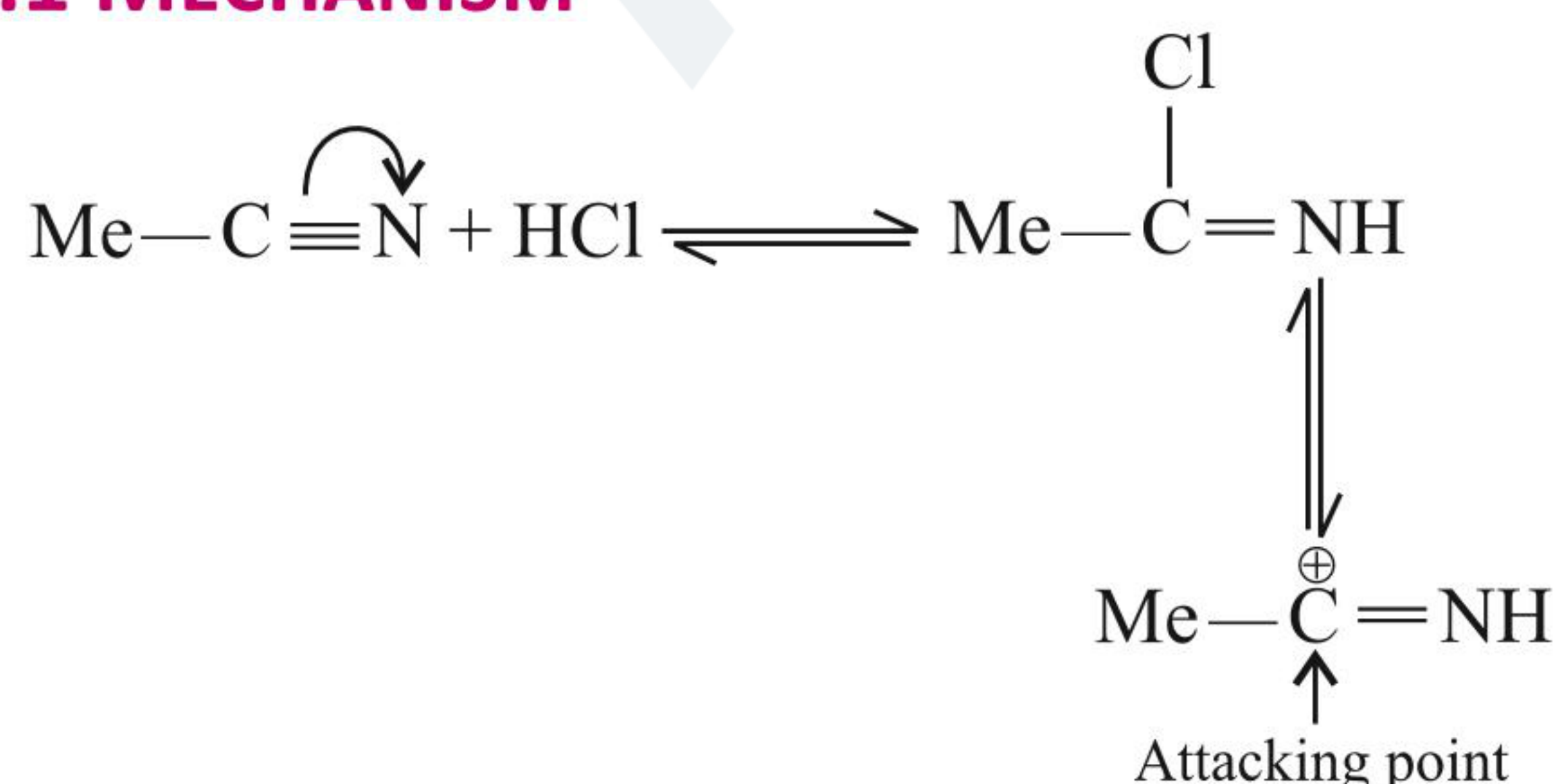
4.19 HOUBEN-HOESCH SYNTHESIS

m-Polyhydroxy phenol + Cyanide + $ZnCl_2/HCl$ gives ketone.



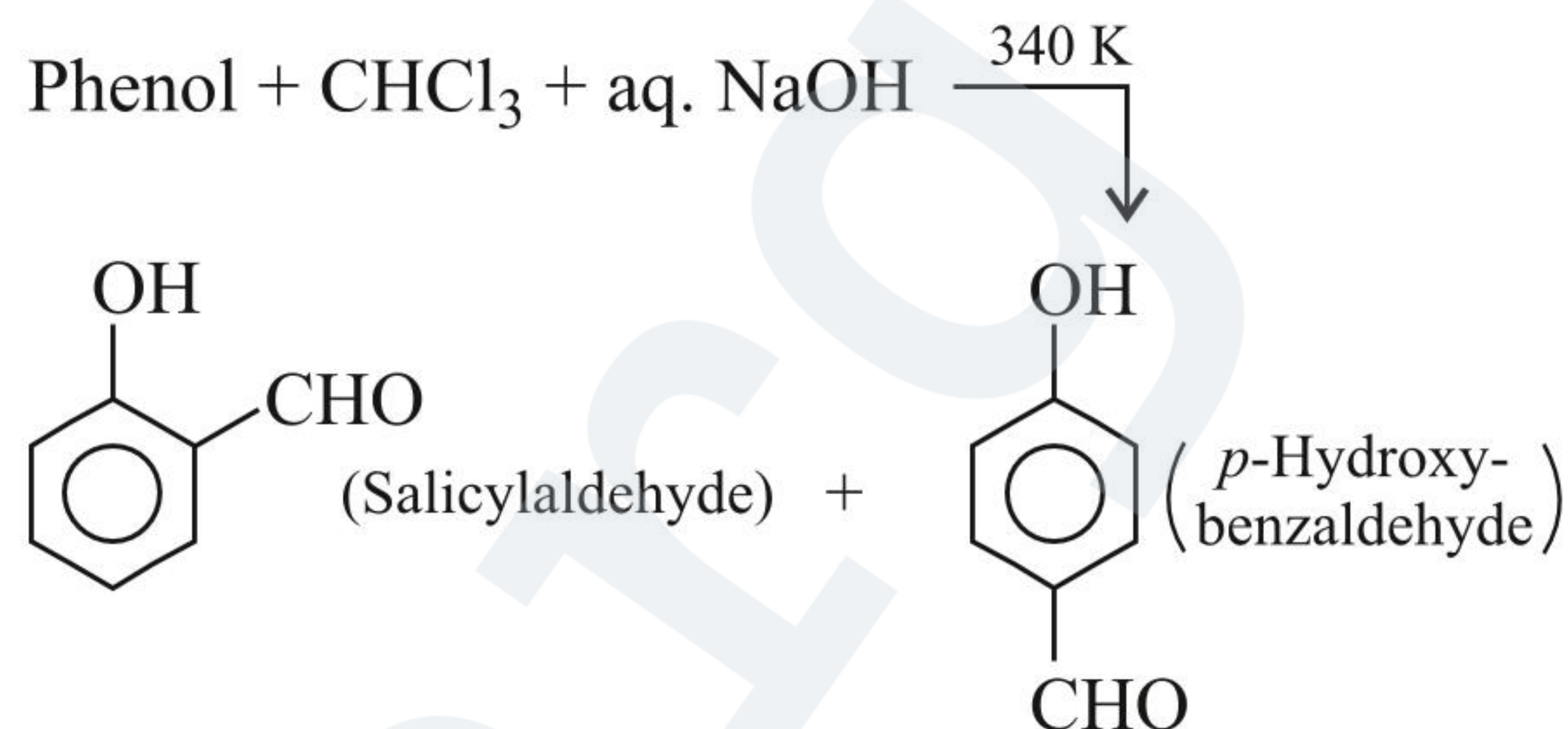
The reaction proceeds *via* the formation of imido chloride.

4.19.1 MECHANISM

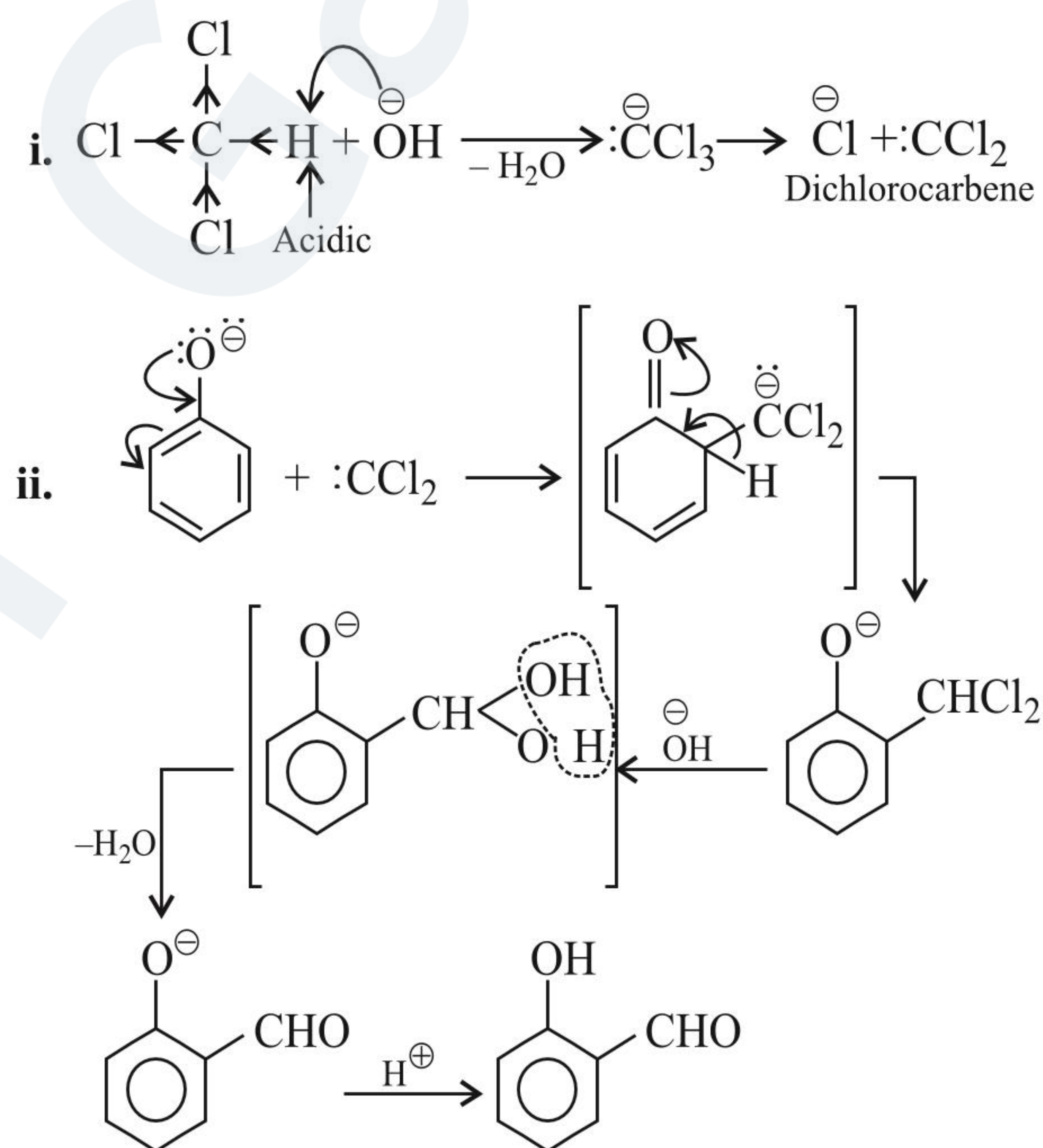


4.20 REIMER-TIEMANN REACTION

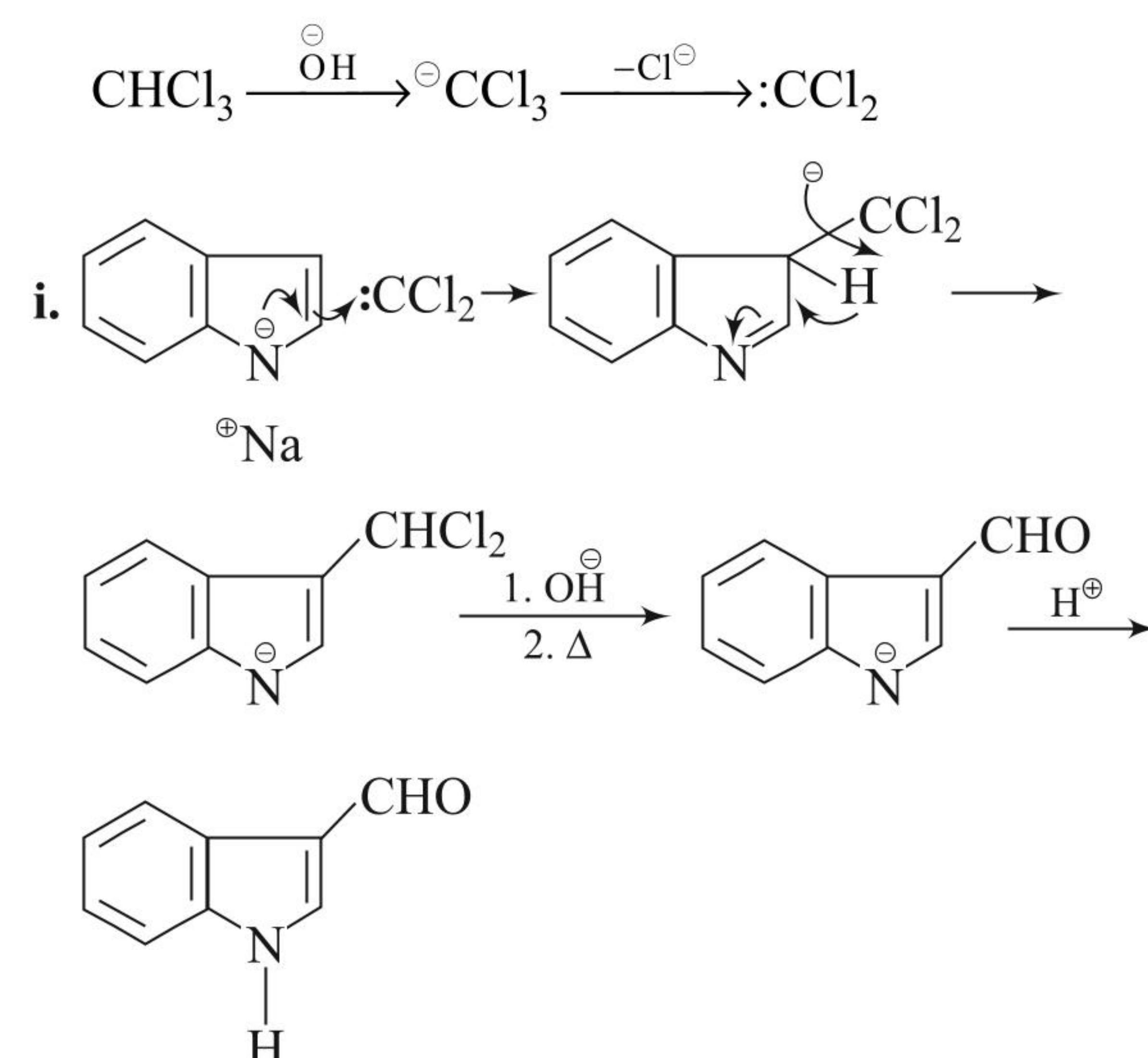
Phenols for aromatic compounds containing EDG when refluxed with $CHCl_3$ and alkali yield *o*- and *p*-hydroxybenzaldehyde. The *ortho* product is the predominant product. It is an electrophilic substitution (SE) on PhO^- ion. The electrophile is dichlorocarbene ($:CCl_2$) which contains a C with only six electrons.

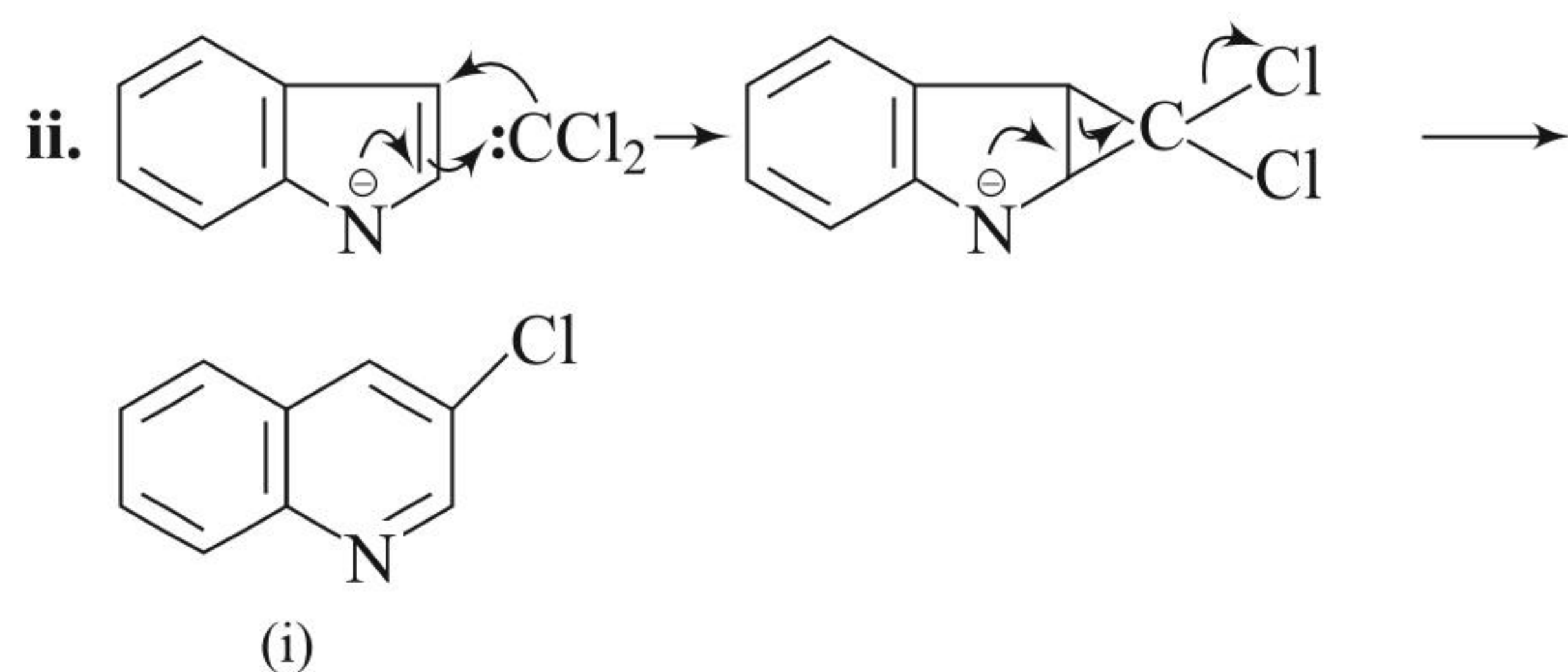


4.20.1 MECHANISM



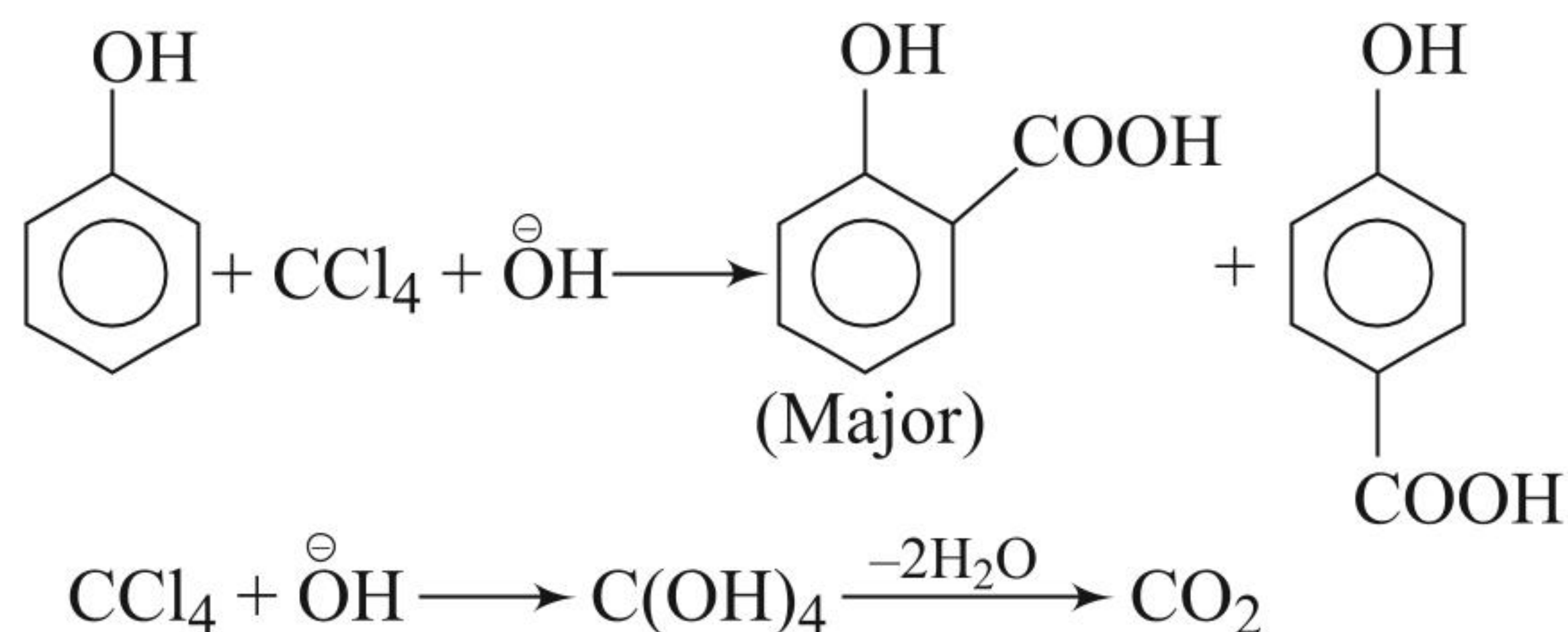
4.20.2 MECHANISM OF THE REIMER TIEMANN REACTION ON INDOLE





4.20.3 EXTENSION OF REIMER-TIEMANN

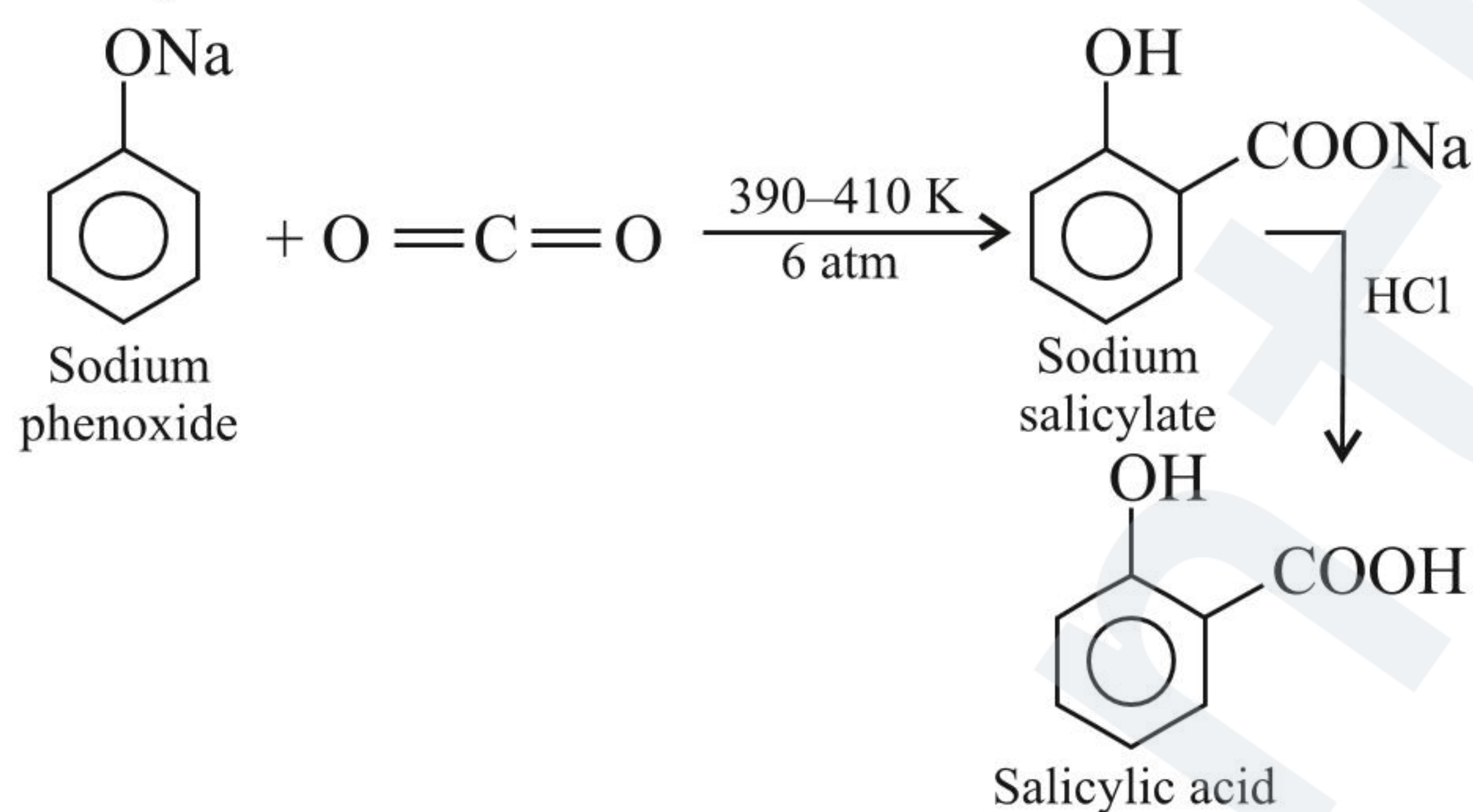
Phenols (or aromatic compounds containing EDG) when refluxed with CX_4 ($X = Cl, Br$ or I) or $CXX'X''X'''$ (different halogens) with base, yield *o*- and *p*-hydroxy benzoic acid.



Thus reaction proceeds with same mechanism as in Kolbe-Schmitt reaction. (see below)

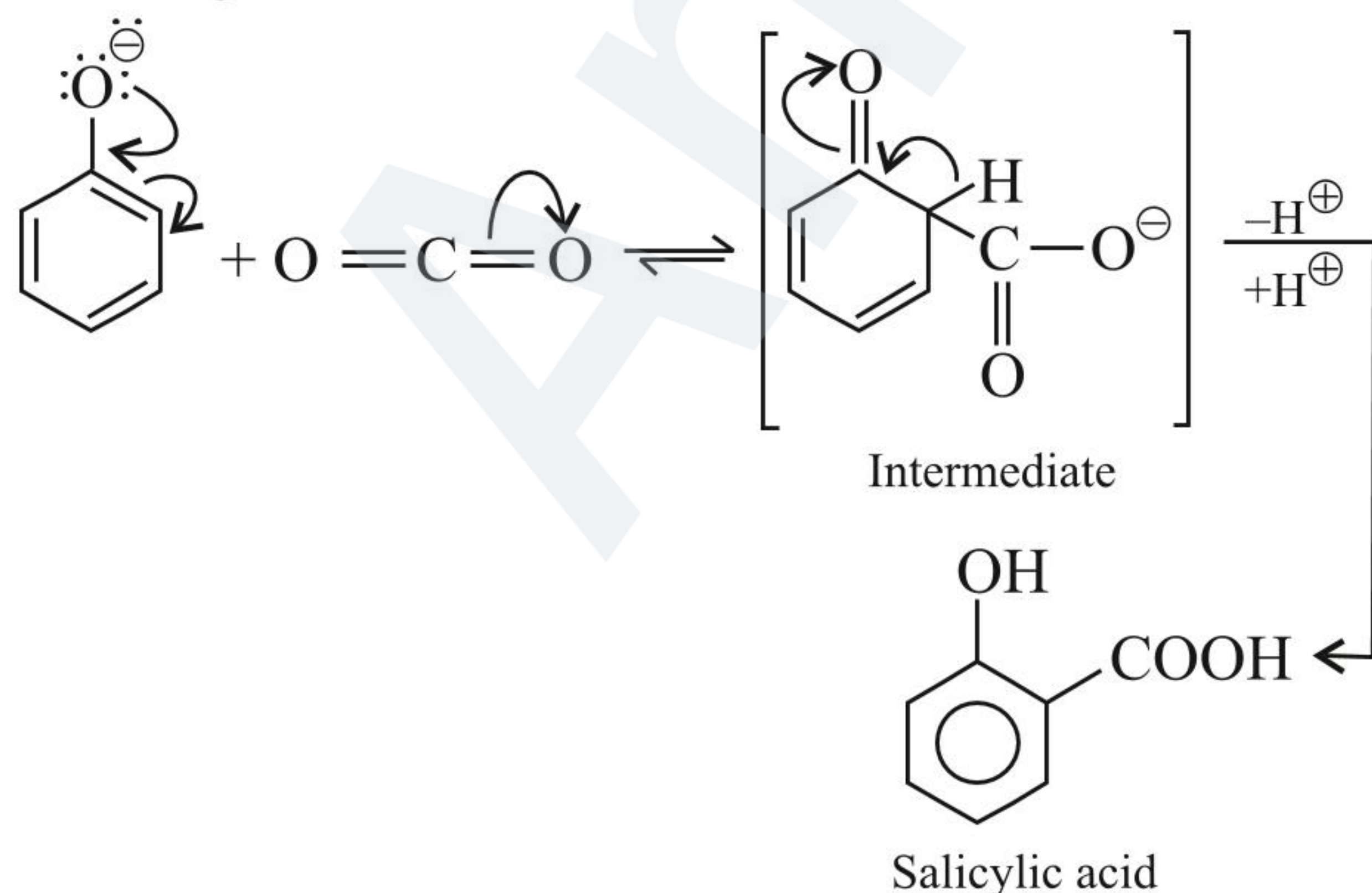
4.21 KOLBE-SCHMITT REACTION

Phenol when heated at (390–410 K) under pressure with CO_2 and alkali gives salicylic acid after acidification in addition to some amount of *p*-isomer.



4.21.1 MECHANISM

CO_2 is a weak electrophile. Nevertheless, it is able to substitute on the strongly activated ring of PhO^- because there is some positive charge on C.



If the temperature is increased to above 430 K or potassium phenoxide is used instead of sodium phenoxide, then *p*-isomer is the main product.

Similarly with CCl_4 and alkali, *o*- and *p*-hydroxy benzoic acids are obtained. The reaction proceeds *via* the formation of CO_2 and the mechanism is same as in Kolbe's reaction.

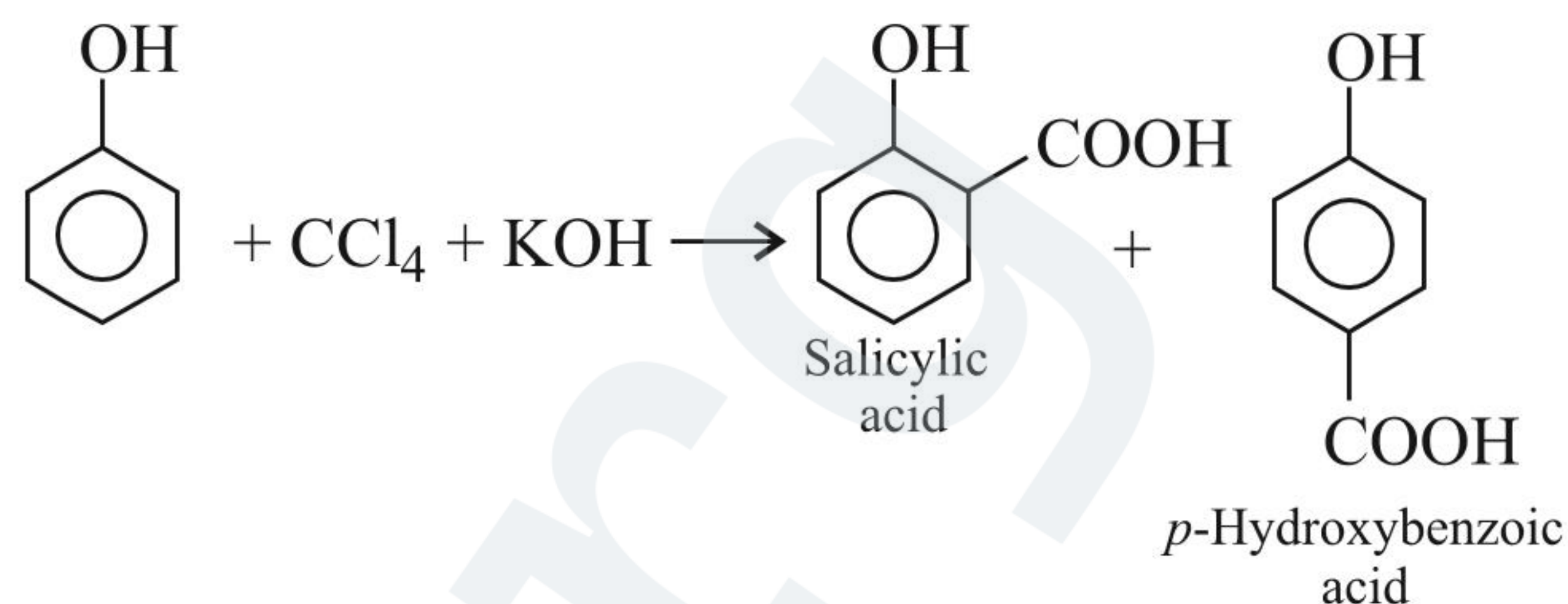
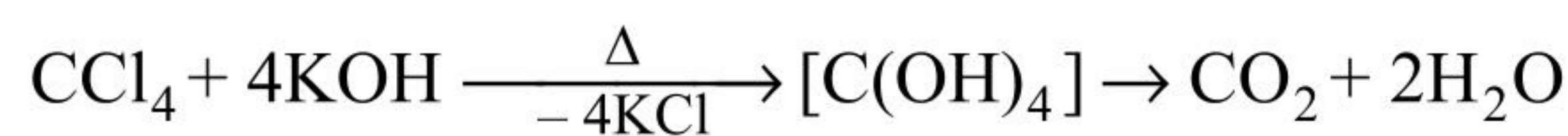
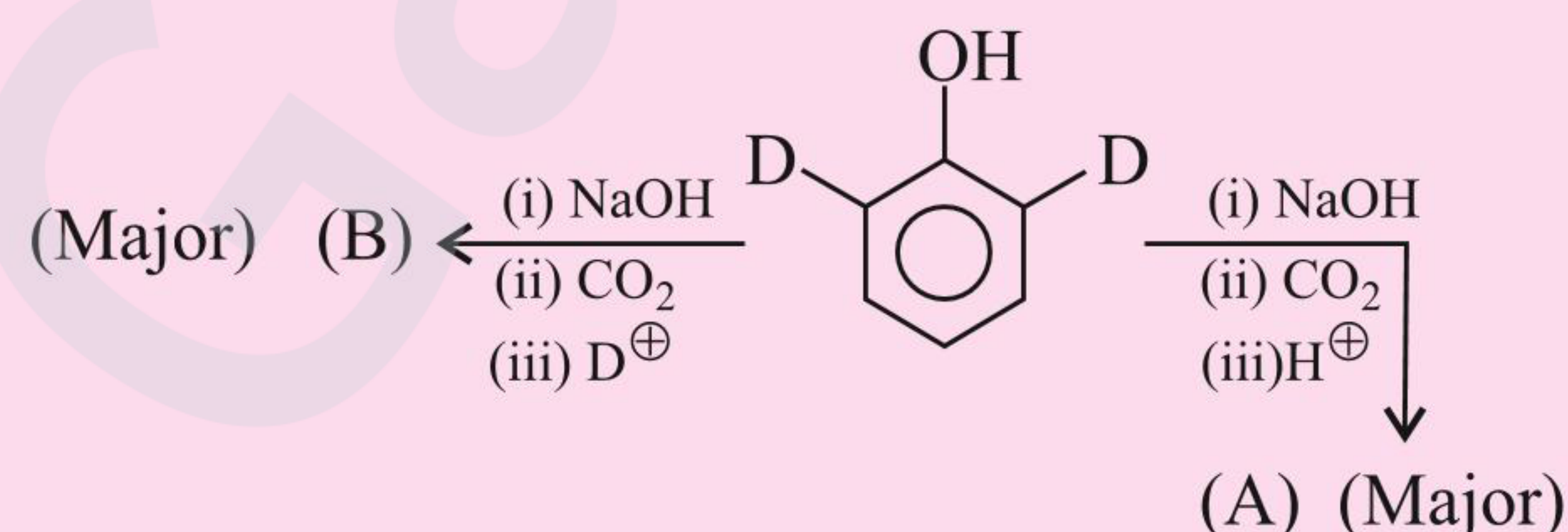


ILLUSTRATION 4.12

Complete the following reaction:



Sol.

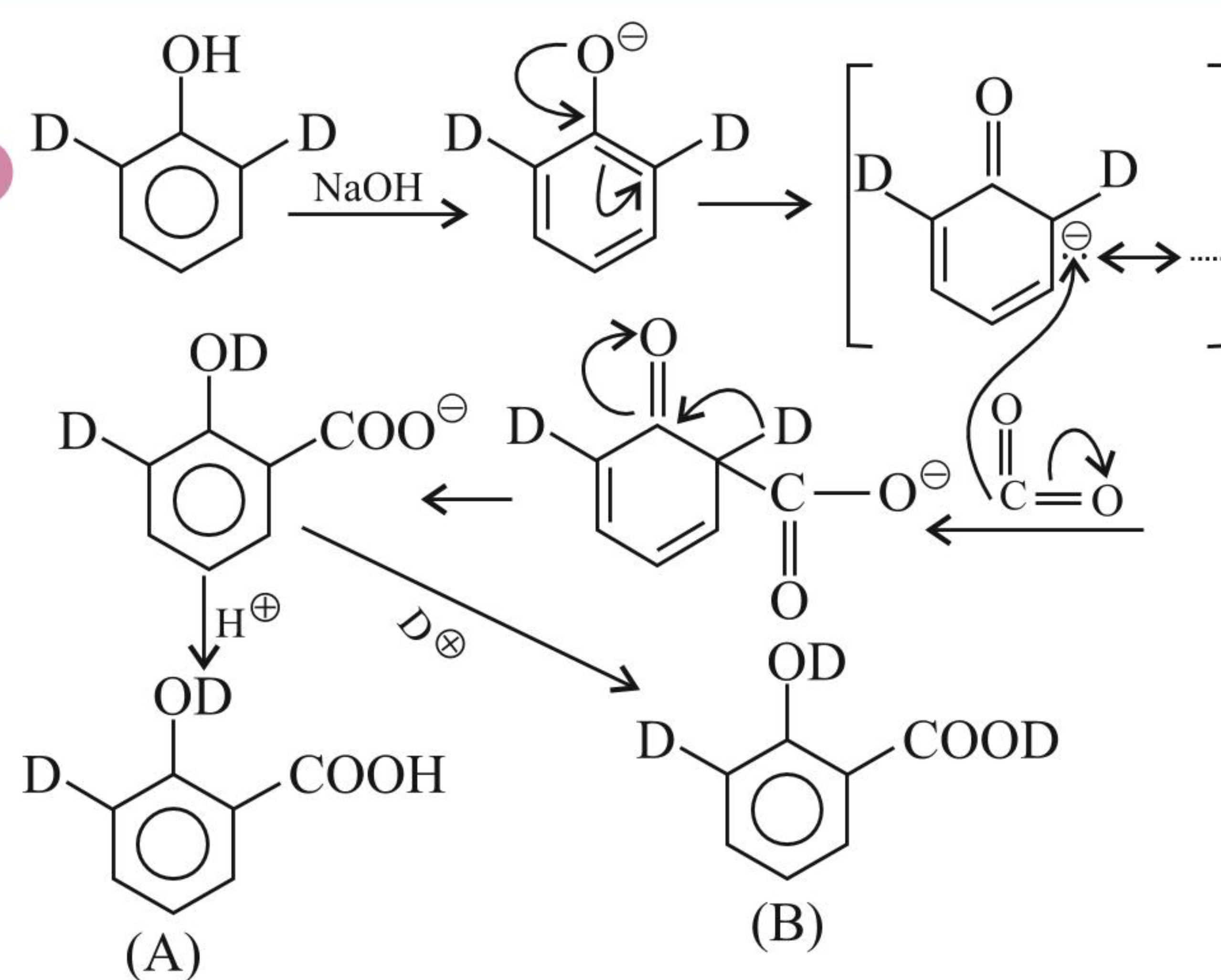
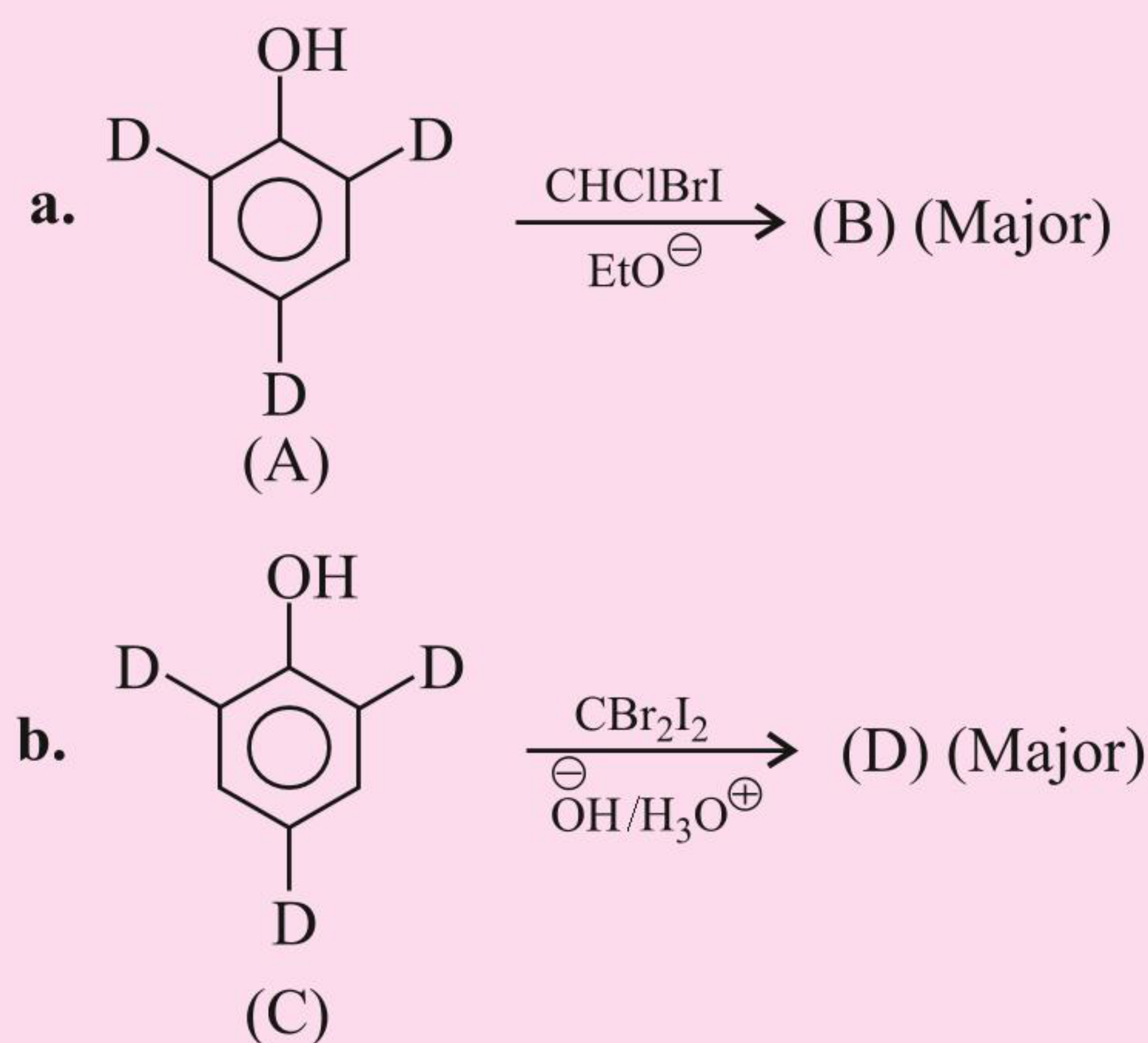
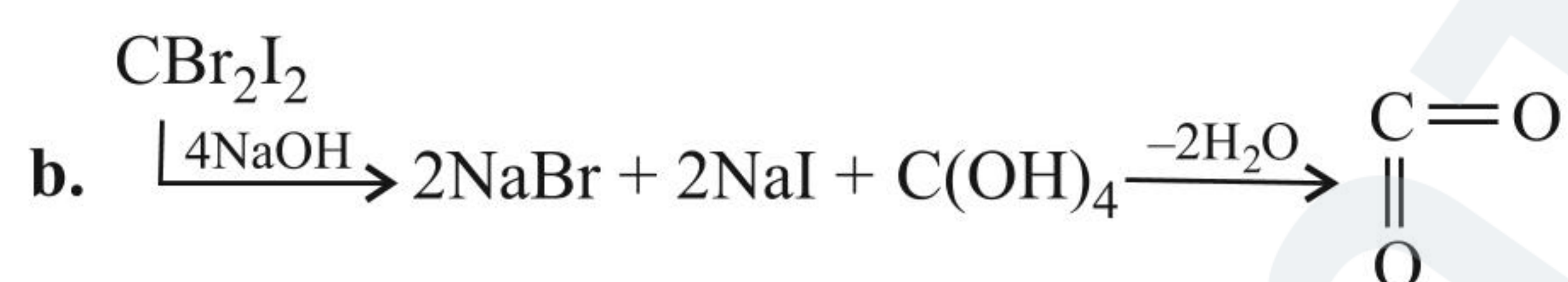
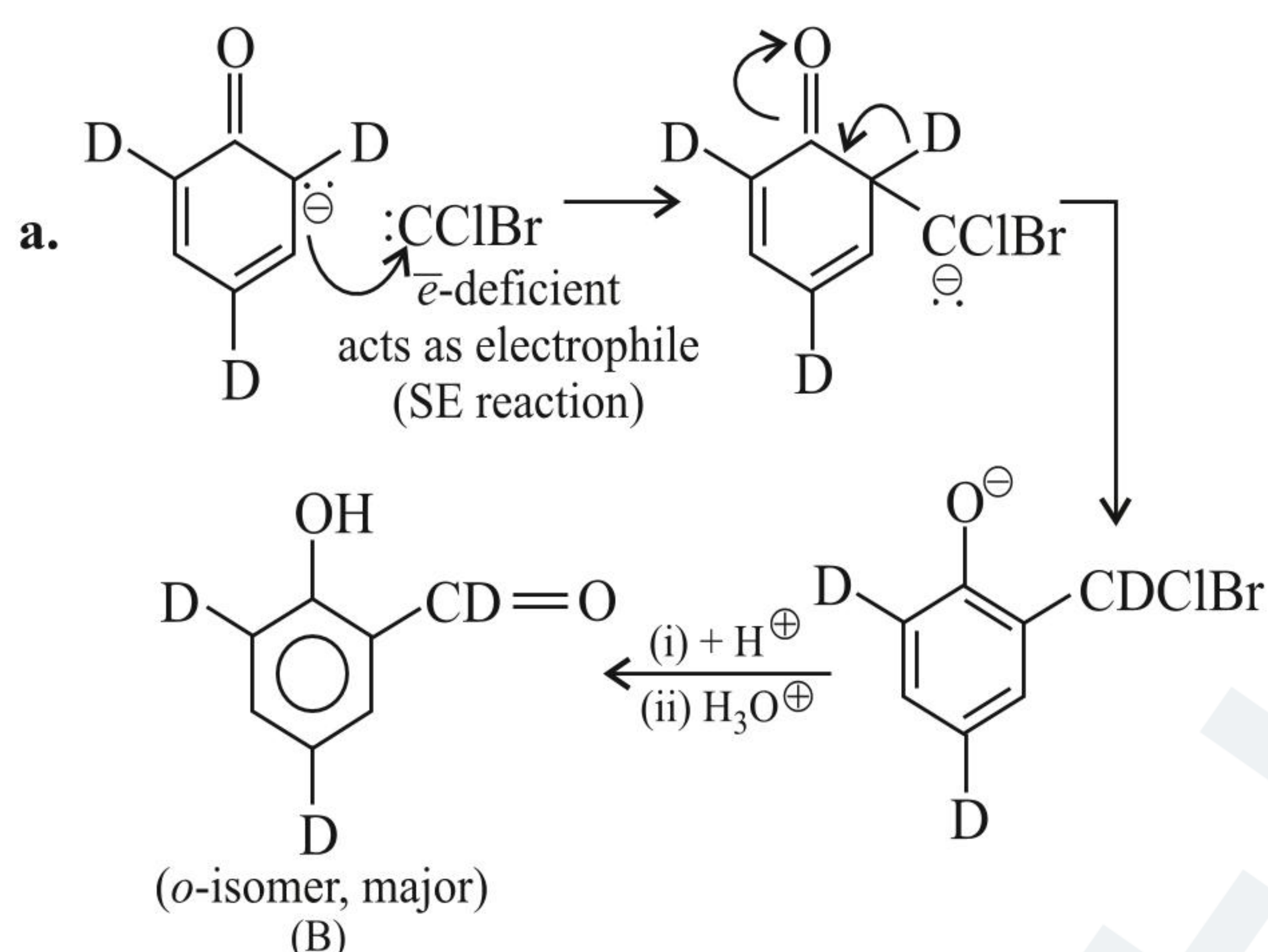
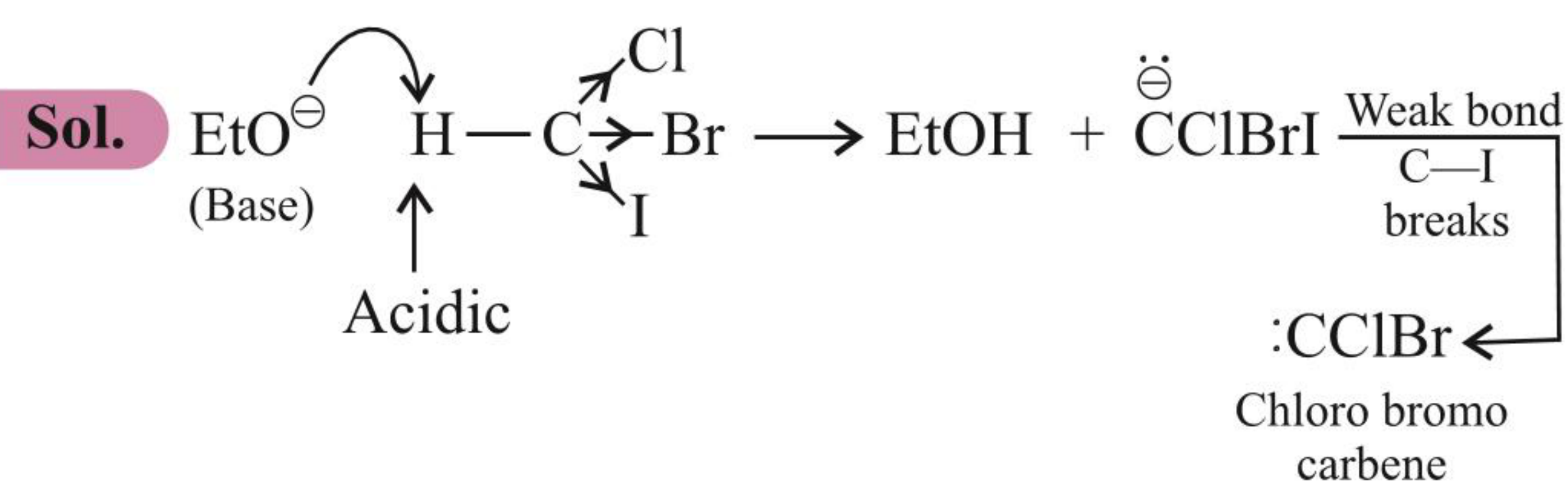
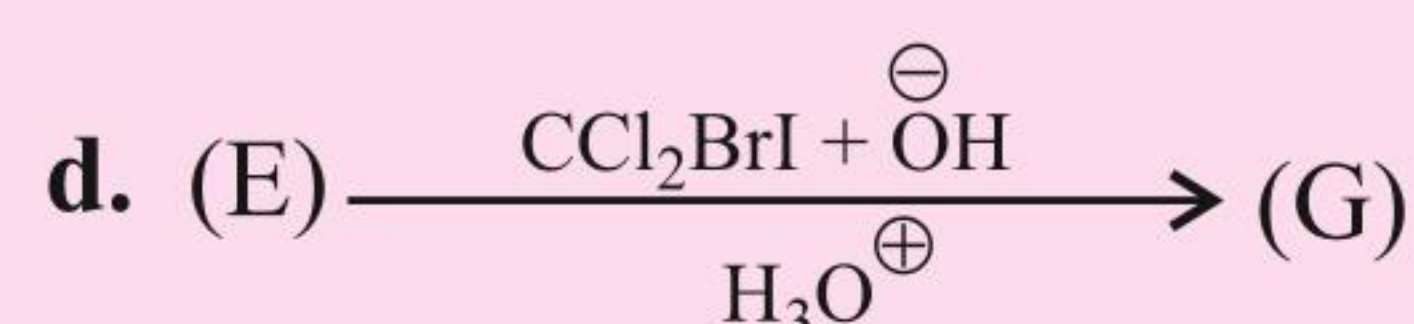
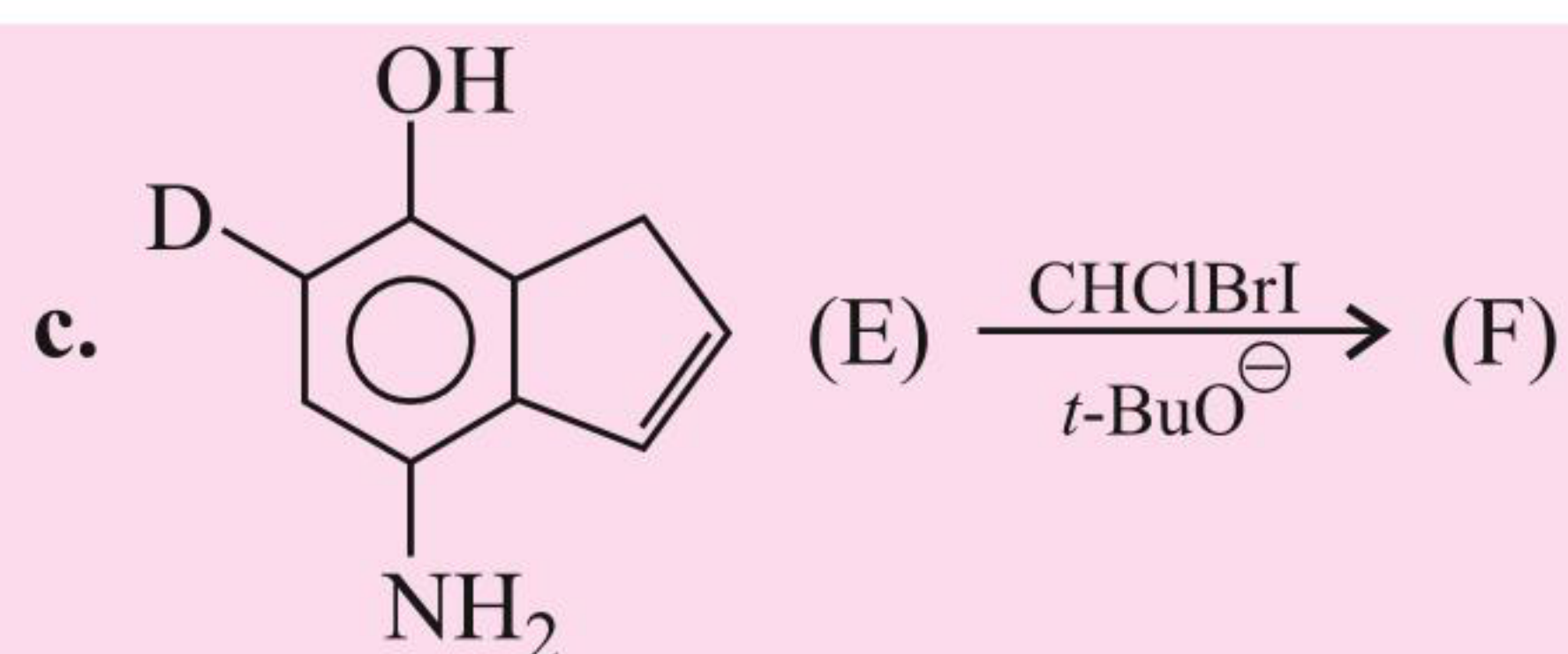


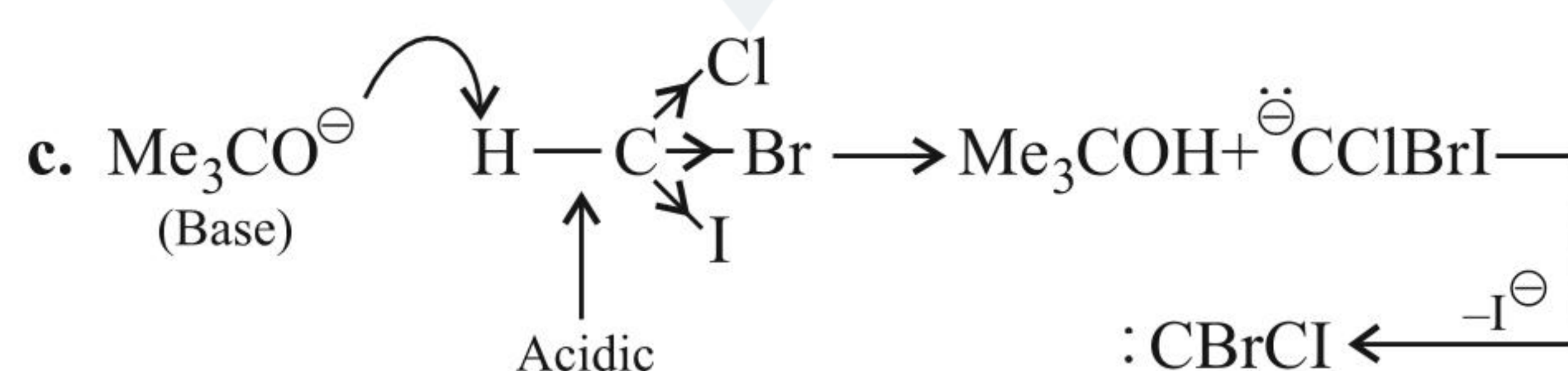
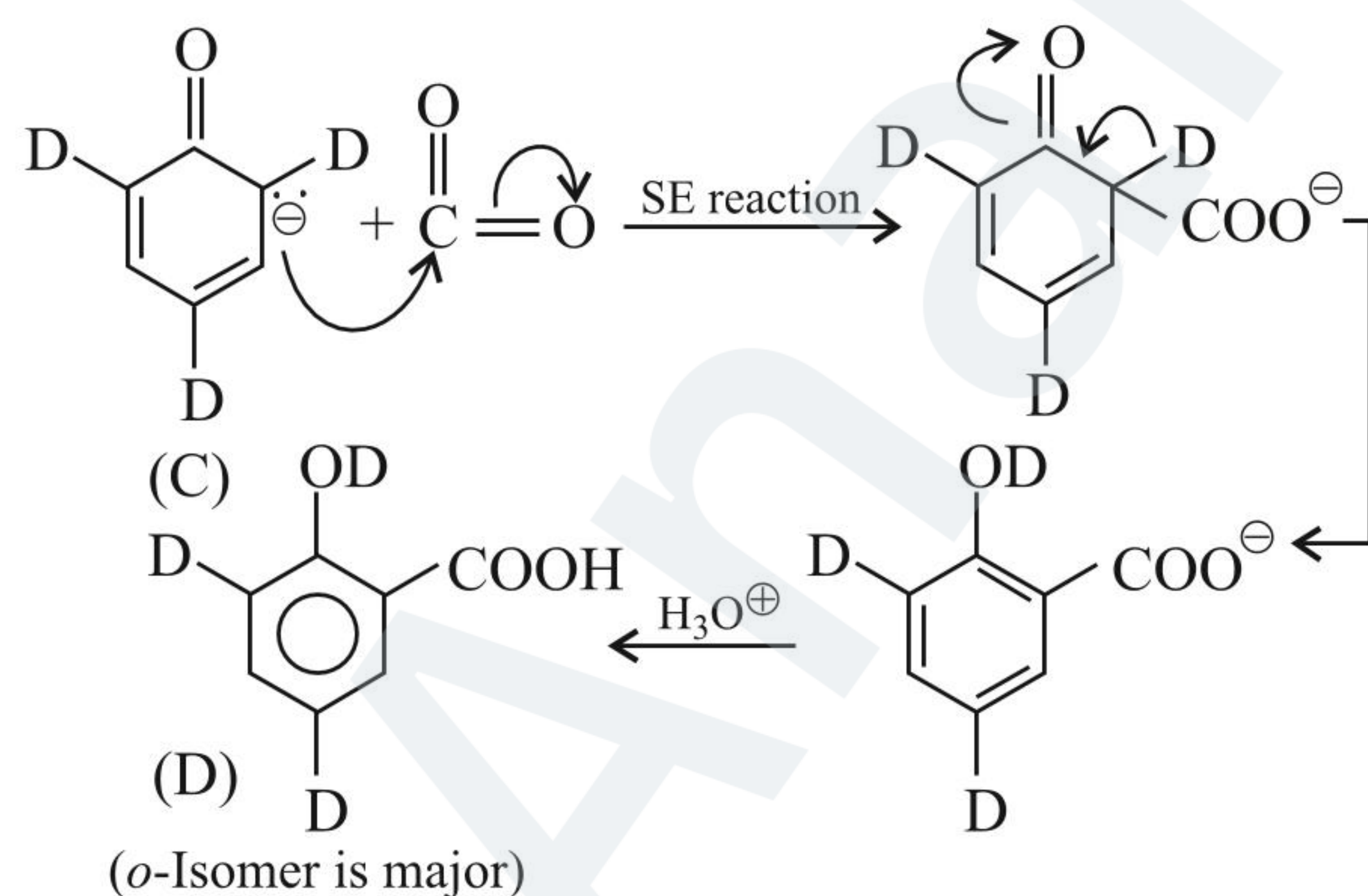
ILLUSTRATION 4.13

Complete the following reactions:





This produces CO_2 ; the reaction is Kolbe reaction.



Carbene also converts $(-NH_2)$ group to $(-N \equiv C-)$ group (Carbylamine reaction) and also adds to $(C=C)$

bond of cyclopentane ring and undergoes Reimer-Tiemann reaction at *o*-position w.r.t. $(-OH)$ group in benzene ring.

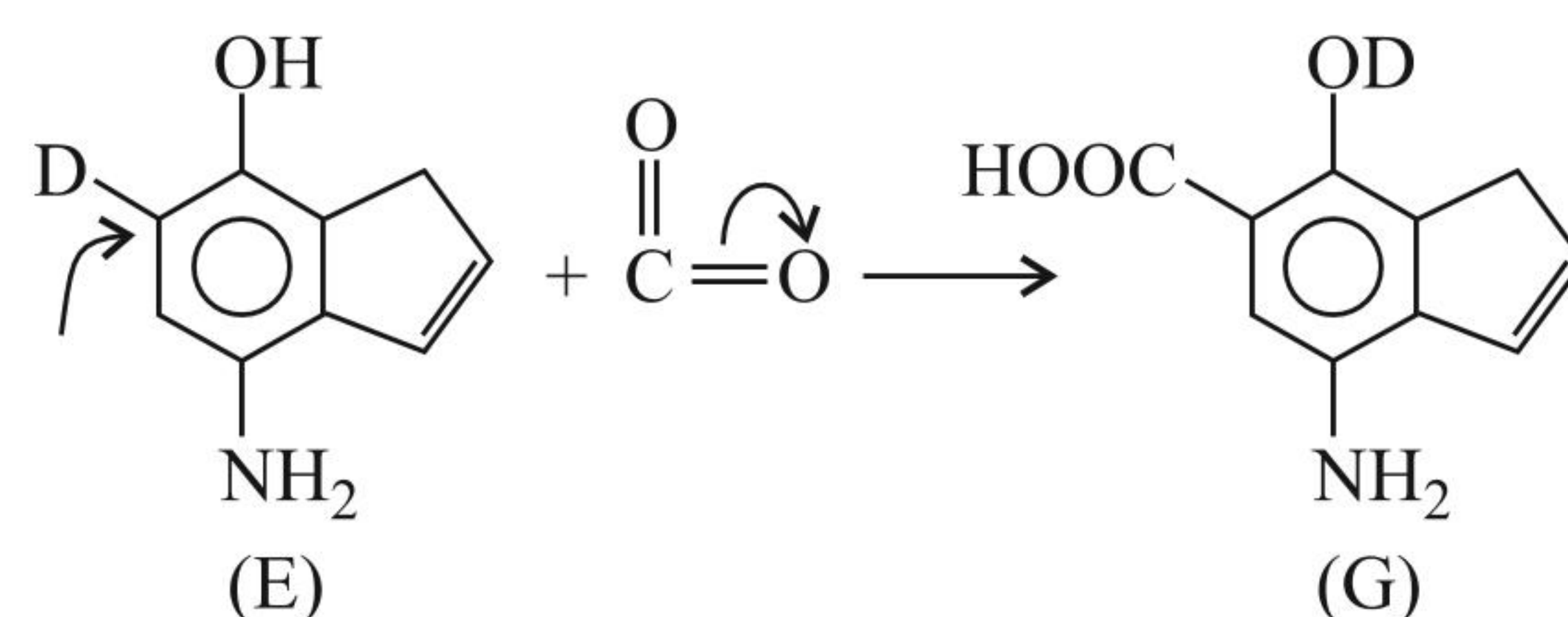
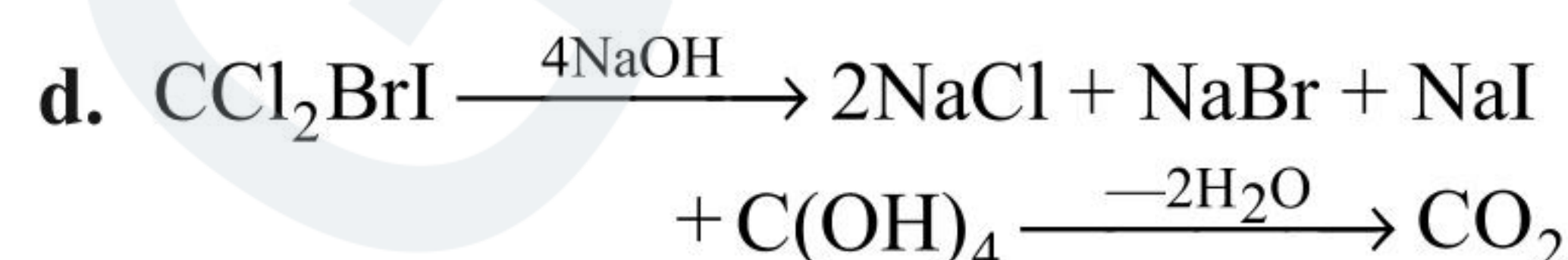
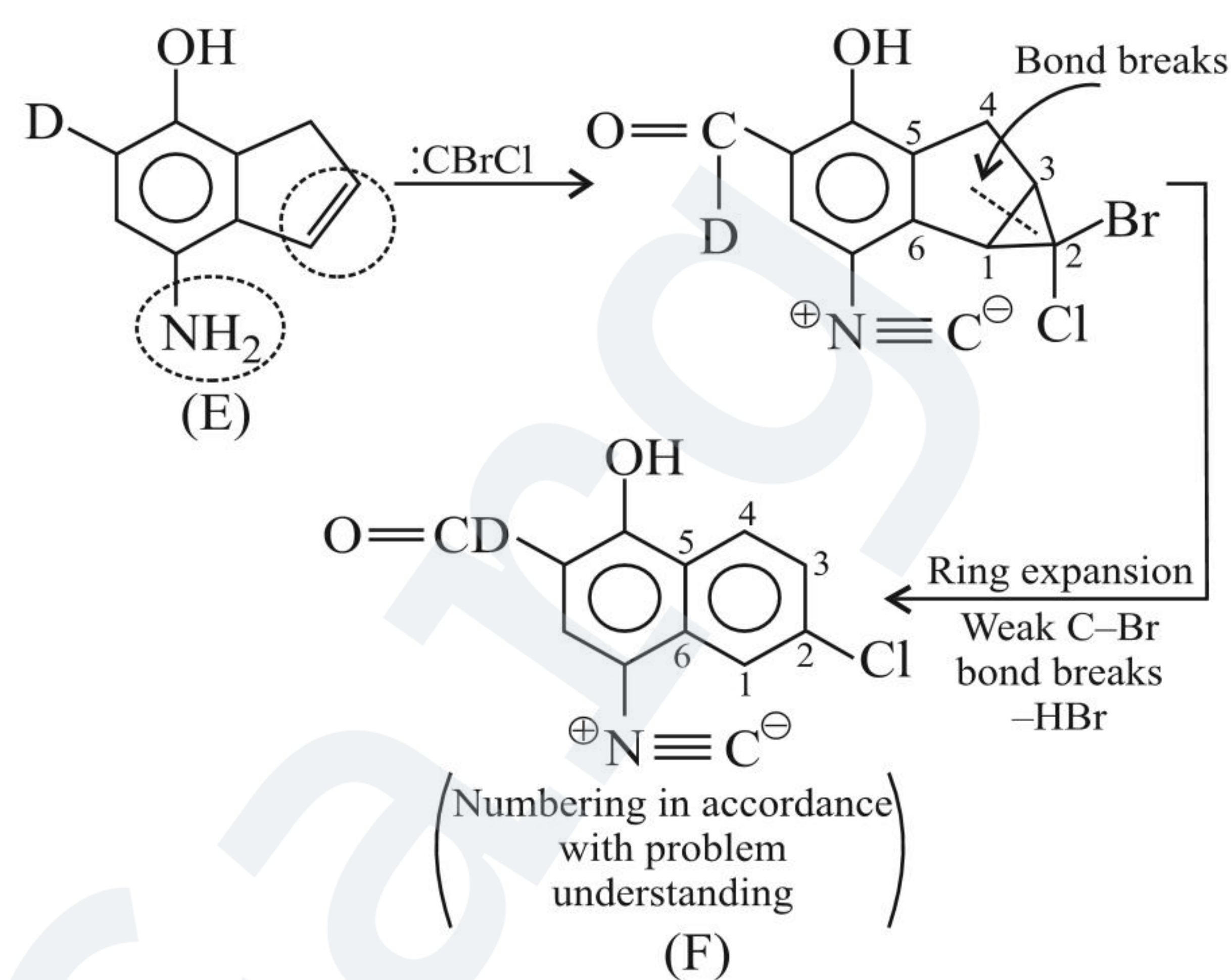
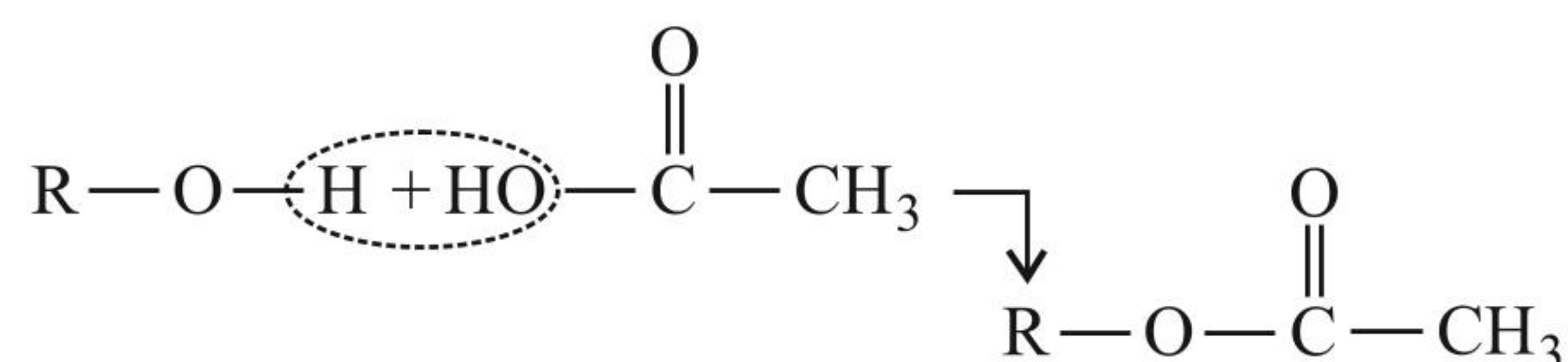


ILLUSTRATION 4.14

0.218 gm of the acetyl derivative of a polyhydric alcohol (molecular mass = 92) requires 0.168 gm of KOH for hydrolysis. Calculate the number of $(-OH)$ groups in the alcohol.

Sol. Let the formula of alcohol is $R(OH)_n$, and the formula of its acetyl derivative is $R(OCOCH_3)_n$.



Molecular mass of $R(OCOCH_3) = (M + 42n)$

M is the molecular mass of alcohol.

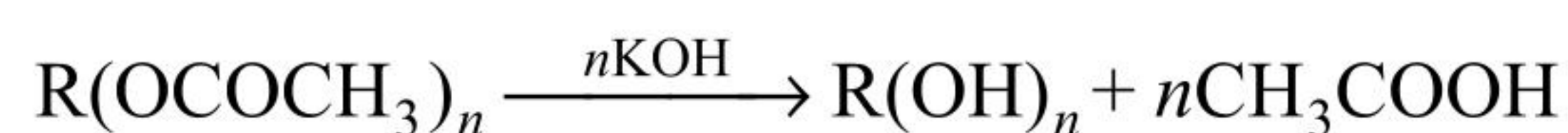
Molecular mass of $(CH_3 - CO -)$ group = 43

One H atom is replaced by (OH) group of CH_3COOH group

Therefore, molecular mass of $R(OCOCH_3)$

$$= [M + (43 - 1)n]$$

$$= (M + 42n)$$



Molecular mass of $nKOH = 56n$

0.218 gm of acetyl derivative requires 0.168 gm of KOH for hydrolysis.

$\therefore (M + 42n)$ gm of acetyl derivative requires

$$= \frac{0.168(M + 42n)}{0.218} = 56n$$

On solving, we get $n = 3$

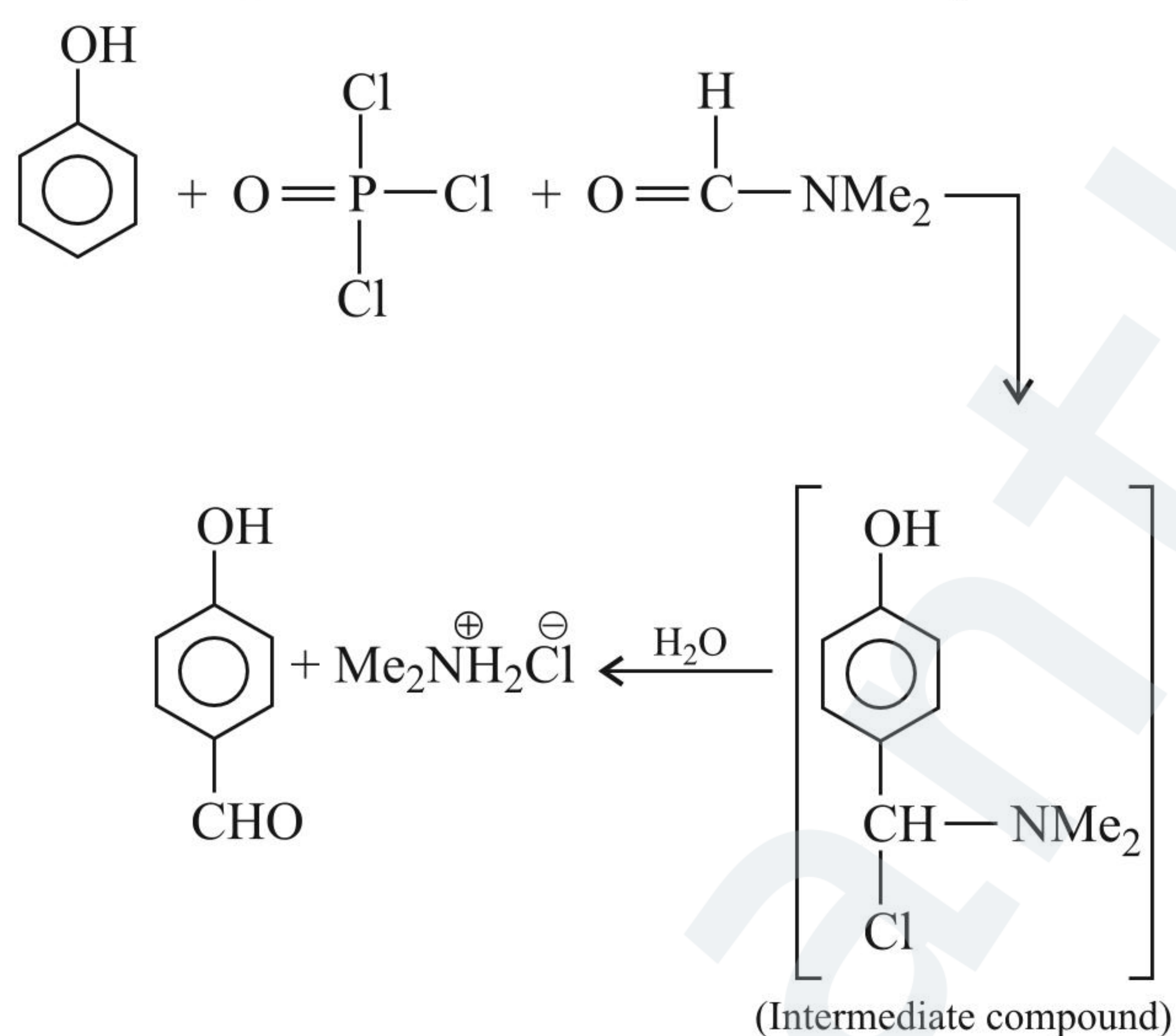
$$\left[\text{Use the formula: } \frac{w(M + 42n)}{W} = 56n \right]$$

w = Weight of KOH, W = weight of acetyl derivative,
 M = Molecular mass of alcohol; n = number of
 ($-\text{OH}$) groups

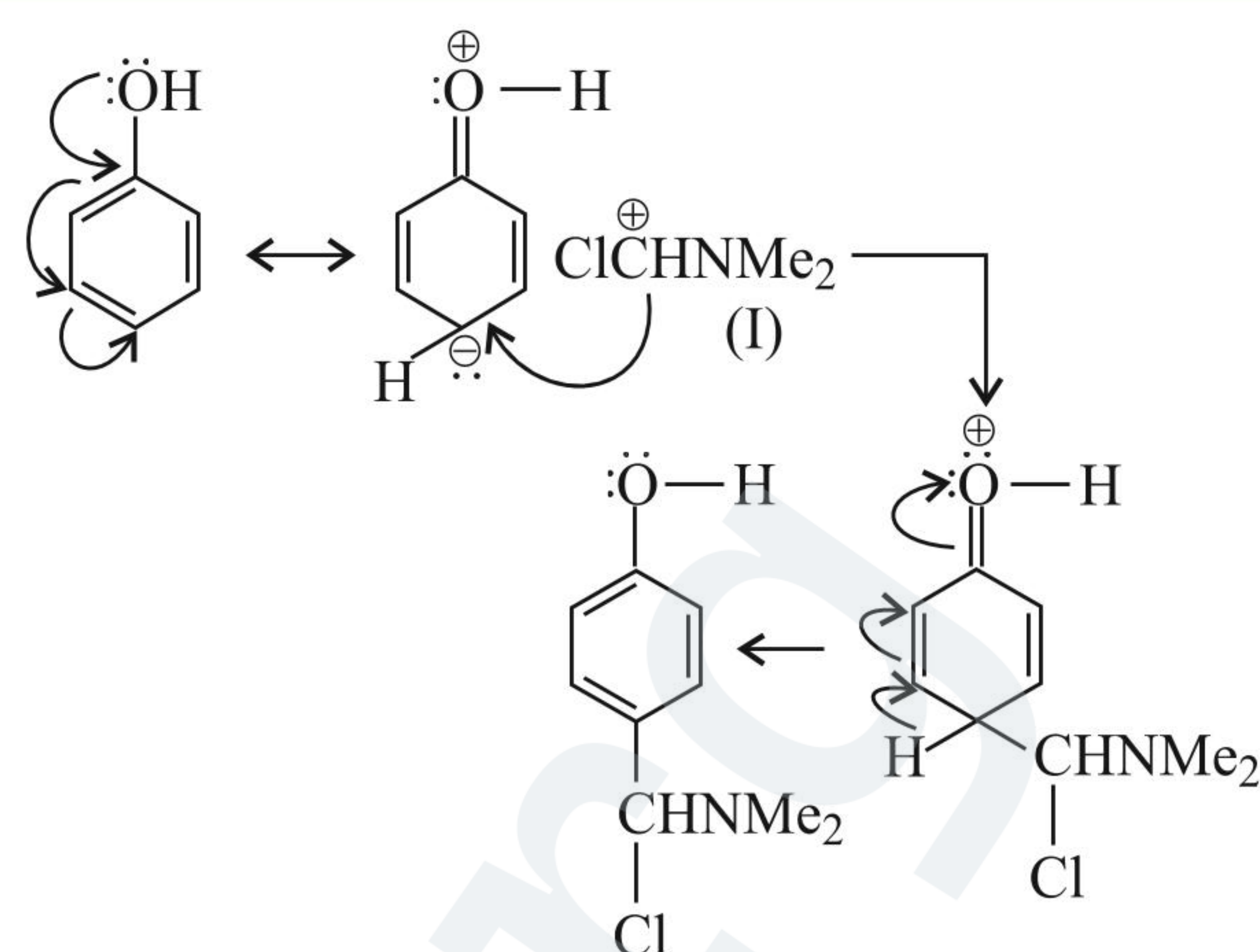
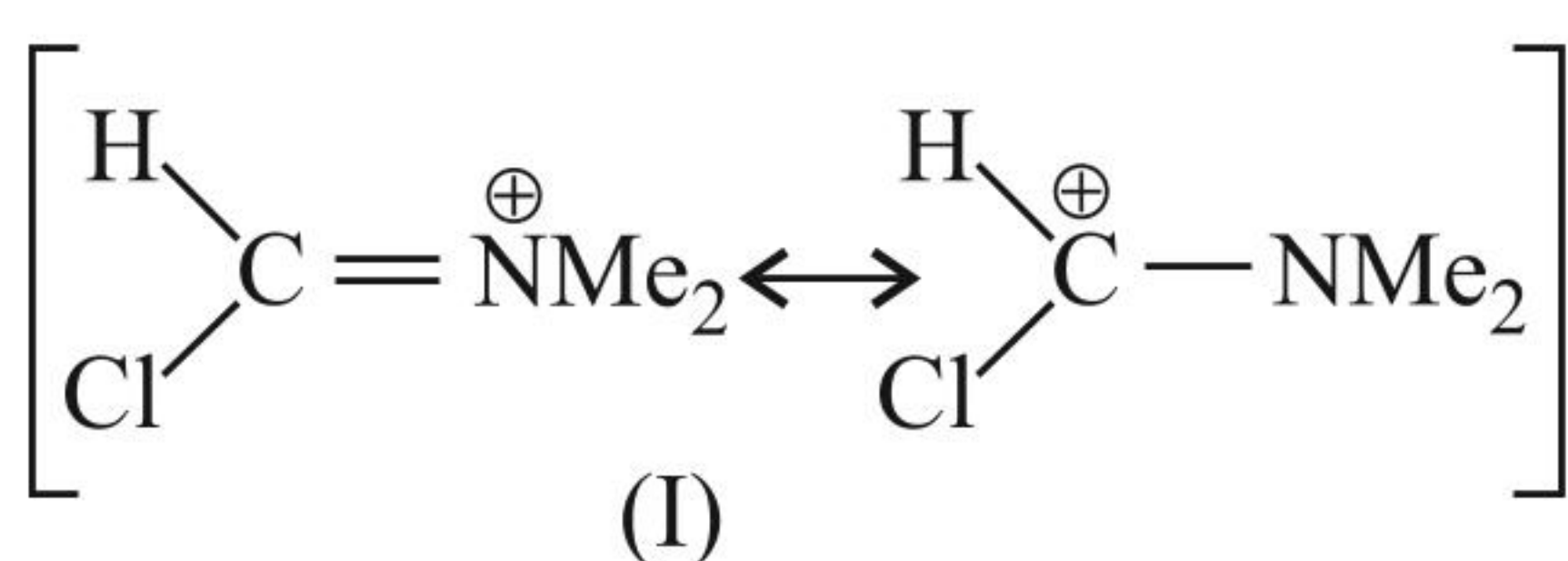
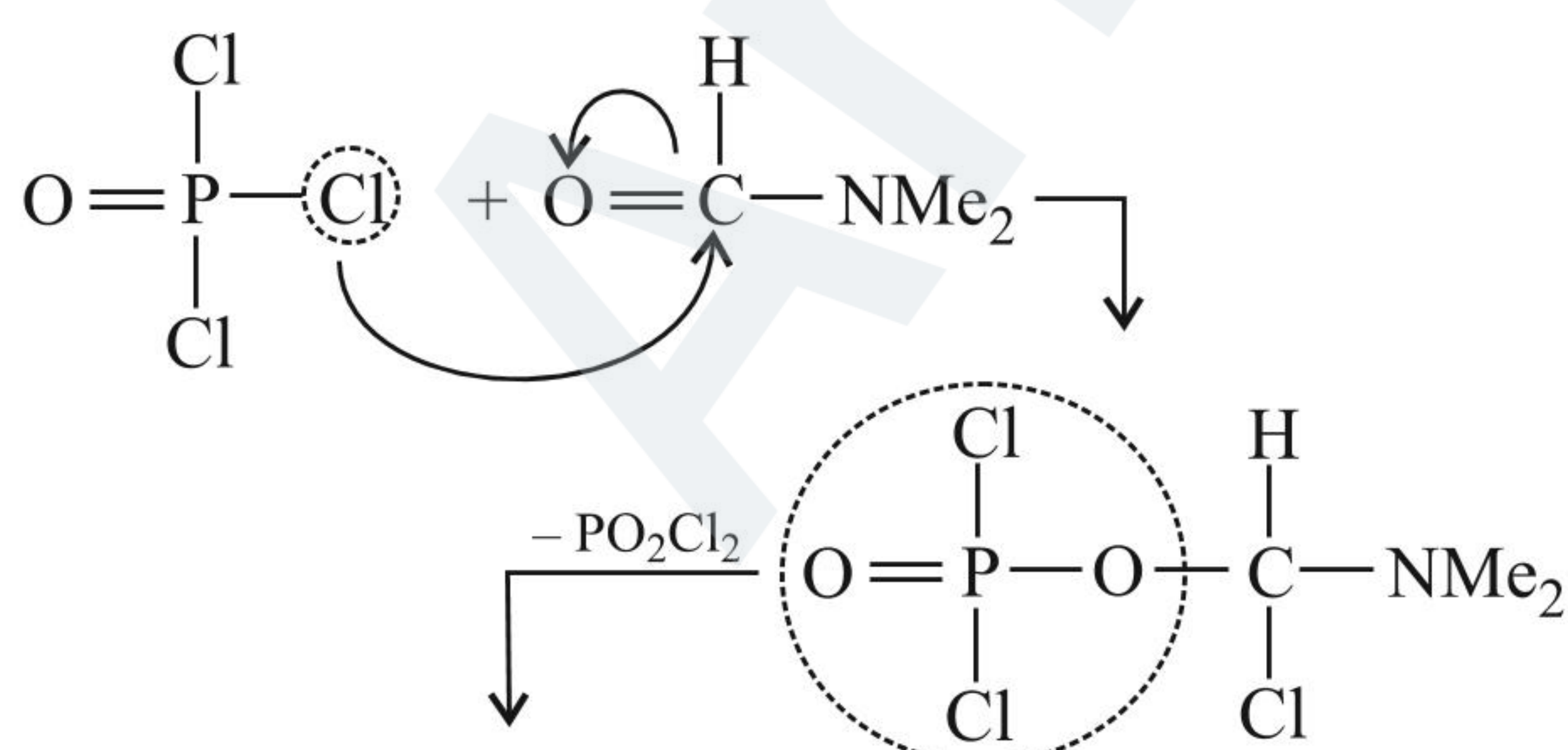
4.22 VILSMEIER REACTION

Phenol with DMF (Dimethyl formamide, $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NMe}_2$) and POCl_3 followed by hydrolysis gives mainly *p*-hydroxy benzaldehyde. This is an example of SE reaction on a highly activated ring such as PhOH.

The electrophile is chloro immonium ion $[\text{Me}_2\text{NCHCl}]^+(\text{I})$

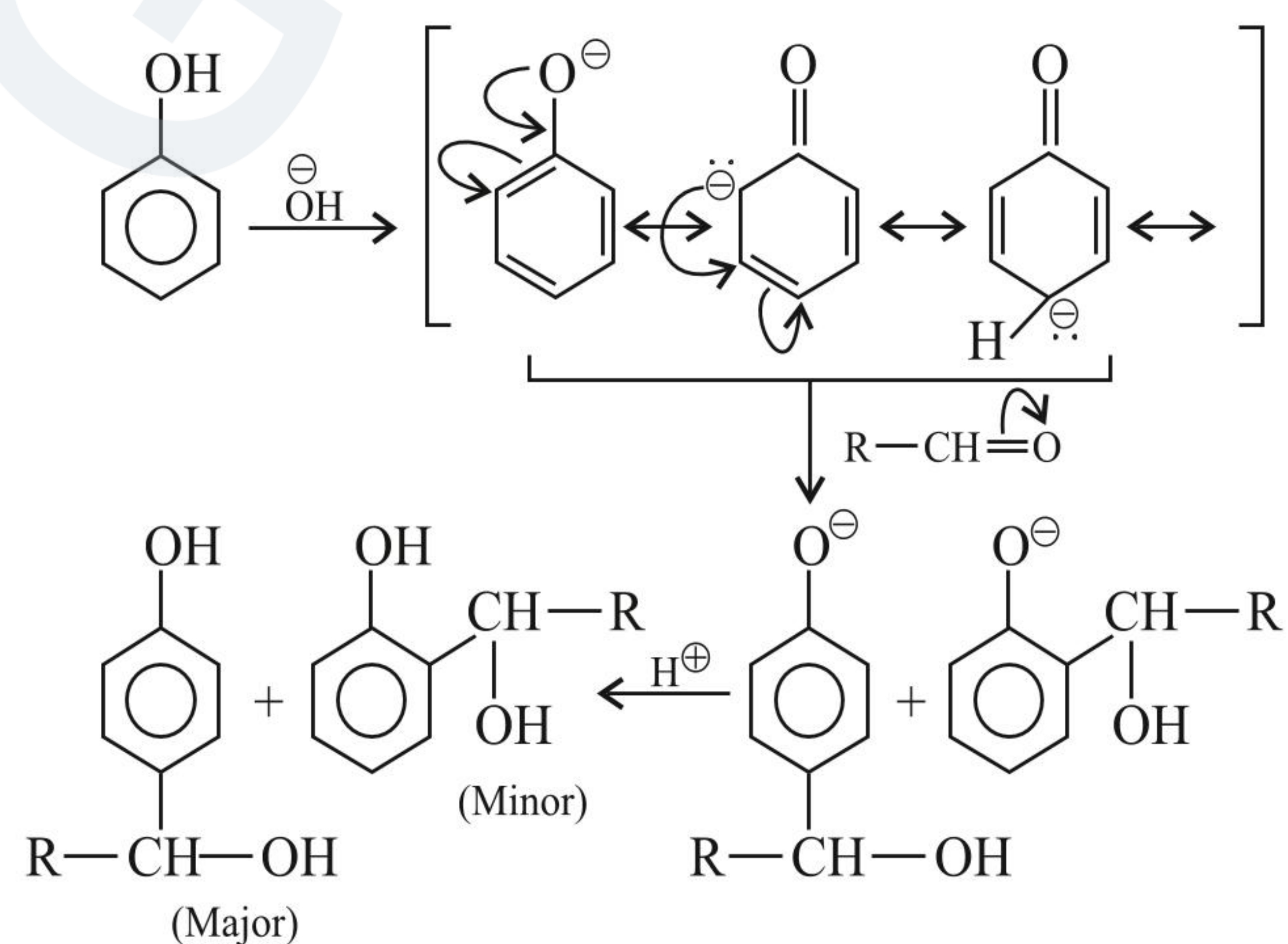


The formation of electrophile (I):

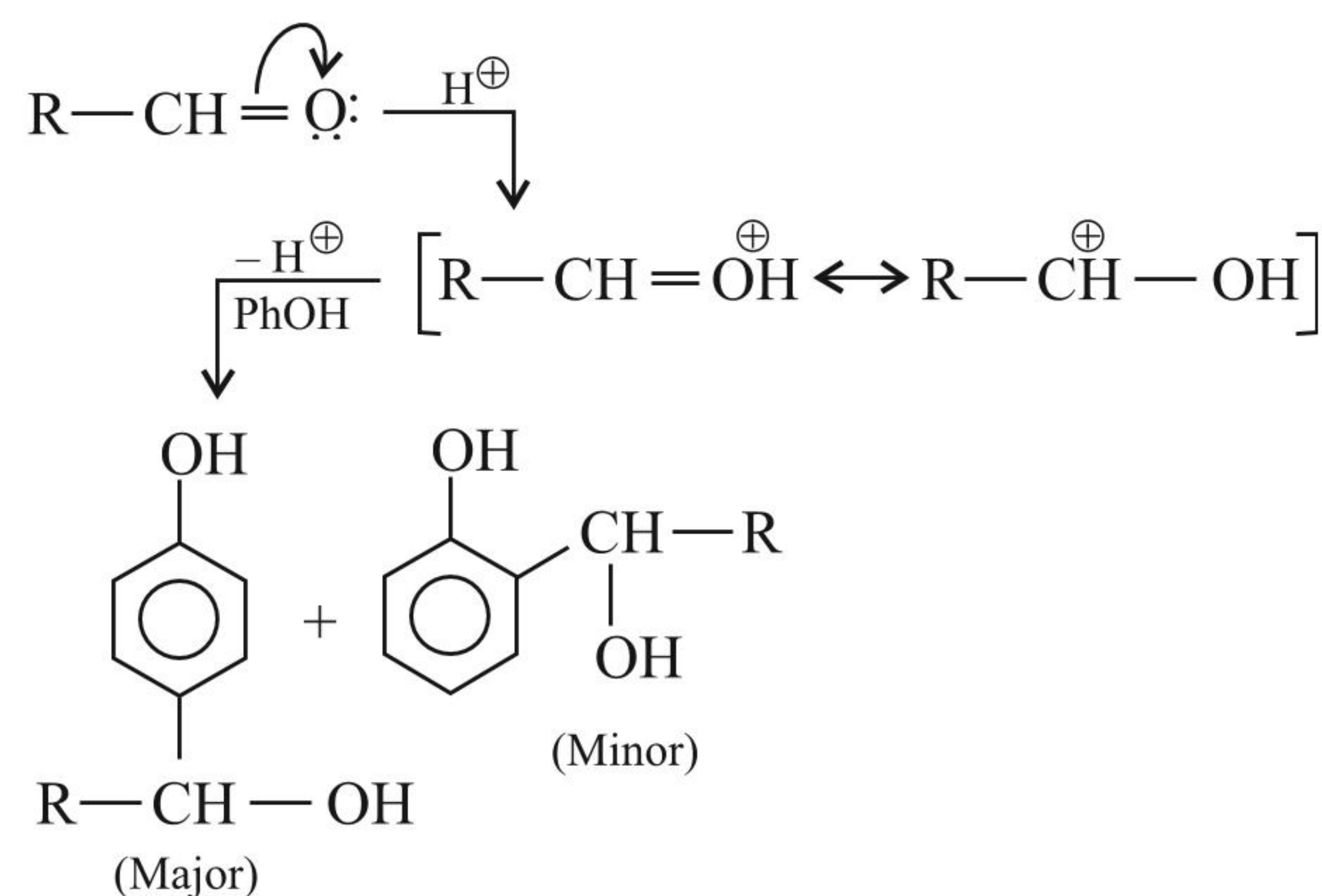


4.23 REACTION OF PHENOL WITH AN ALDEHYDE

- a. Base-catalysed reaction followed by acidification reaction of 1 mol of PhOH with 1 mol of an aldehyde:

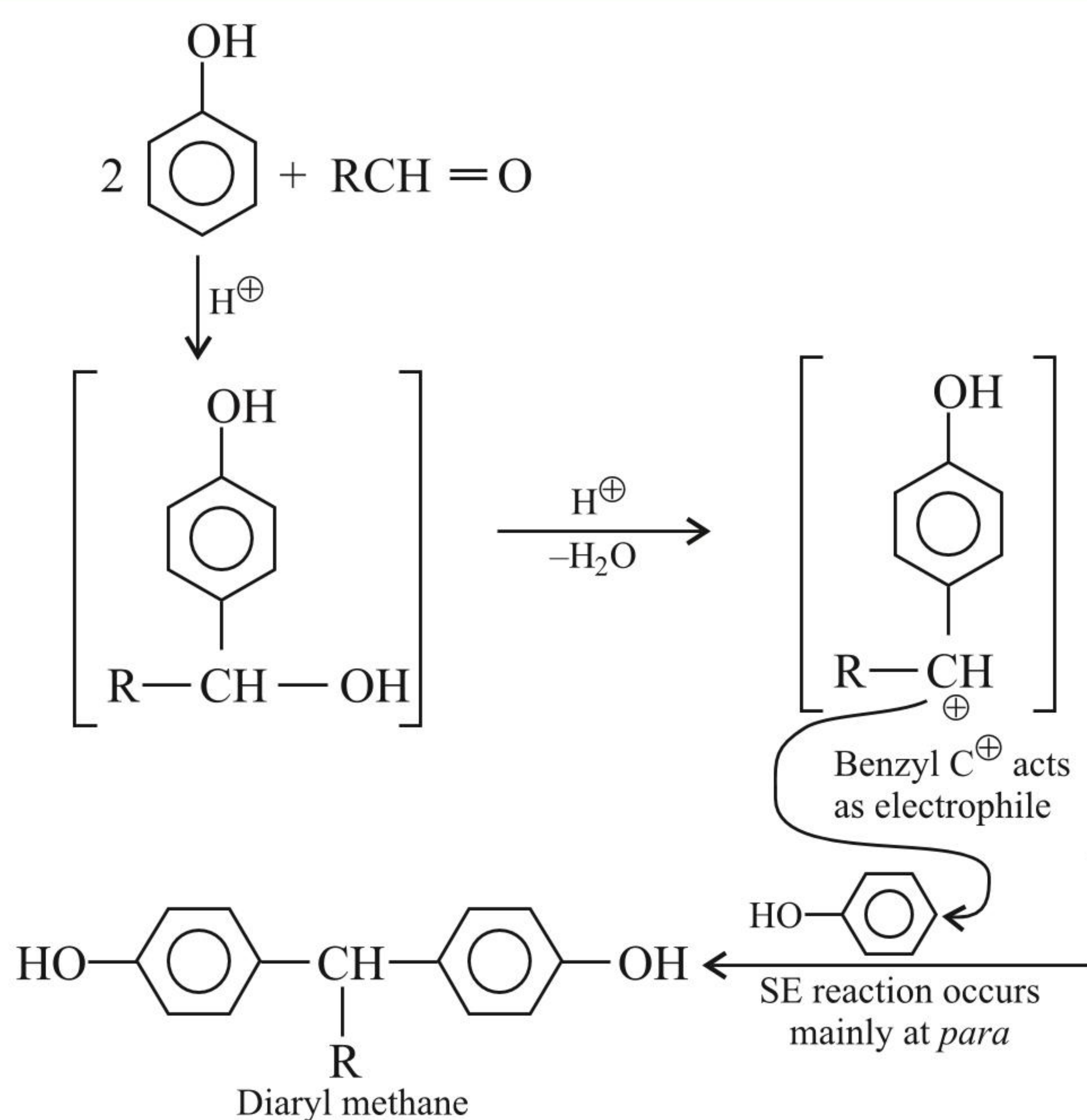


- b. Acid-catalysed reaction of 1 mol of PhOH with 1 mol of an aldehyde:



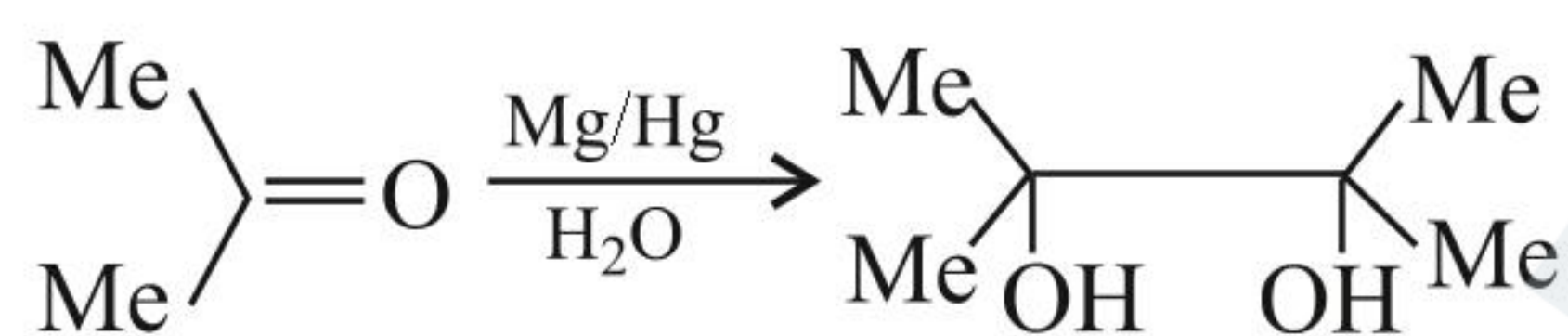
In both conditions (a) and (b), the same product is formed but in (a) PhO^- is the active substrate, whereas in (b) PhOH is the active substrate.

- c. Acid-catalysed reaction of 2 mol of PhOH with 1 mol of an aldehyde:



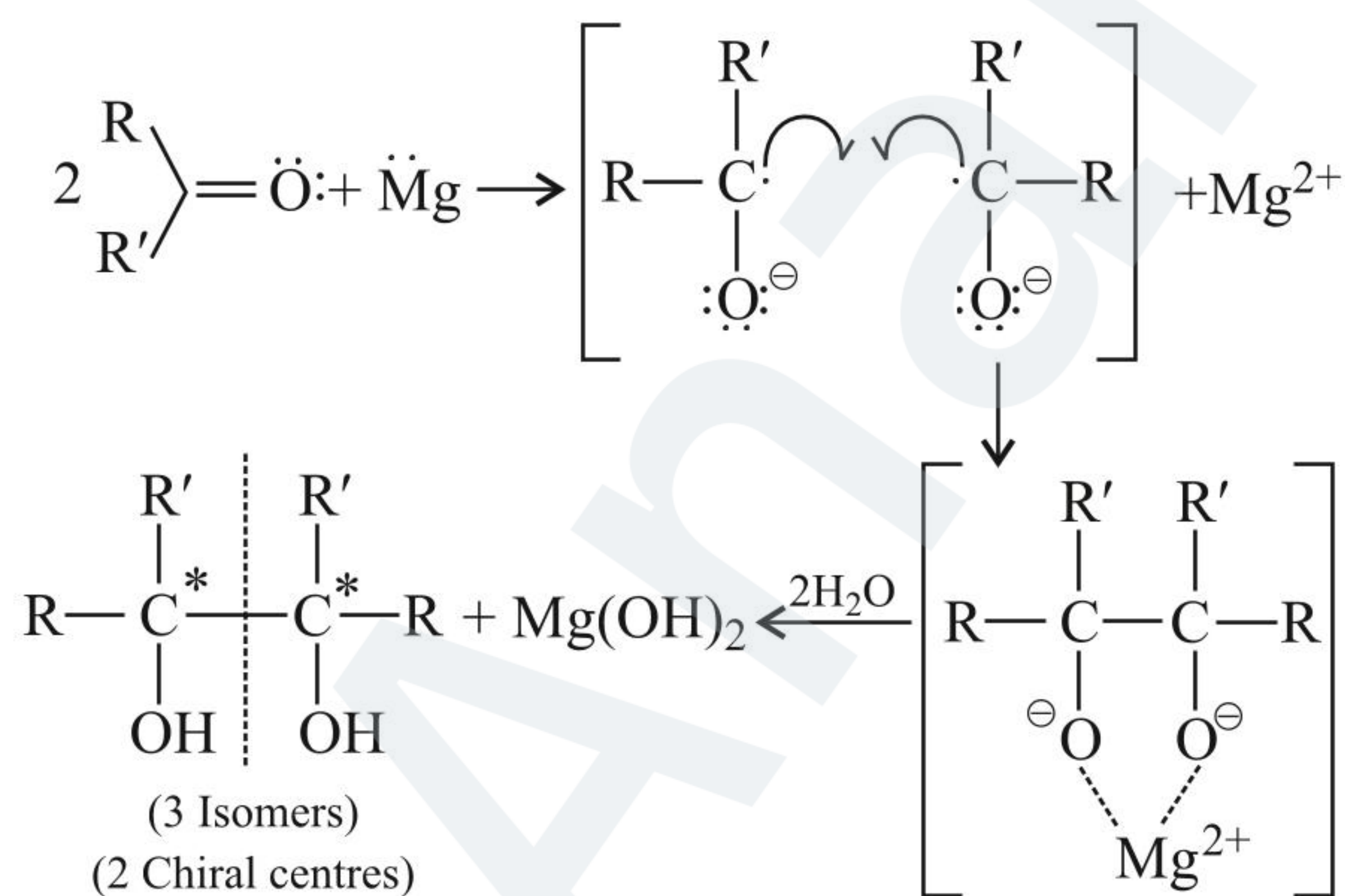
4.24 BIMOLECULAR REDUCTION OF CARBONYL COMPOUND TO VICINAL DIOL

Formation of pinacol: Carbonyl compounds on reduction with Mg amalgam, followed by acid hydrolysis form vicinal diol, called pinacol. For example,



4.24.1 MECHANISM

Electron transfer from Mg to ($\text{>C}=\text{O}$) occurs, giving a **radical anion** or ketyl, followed by dimerisation and hydrolysis.

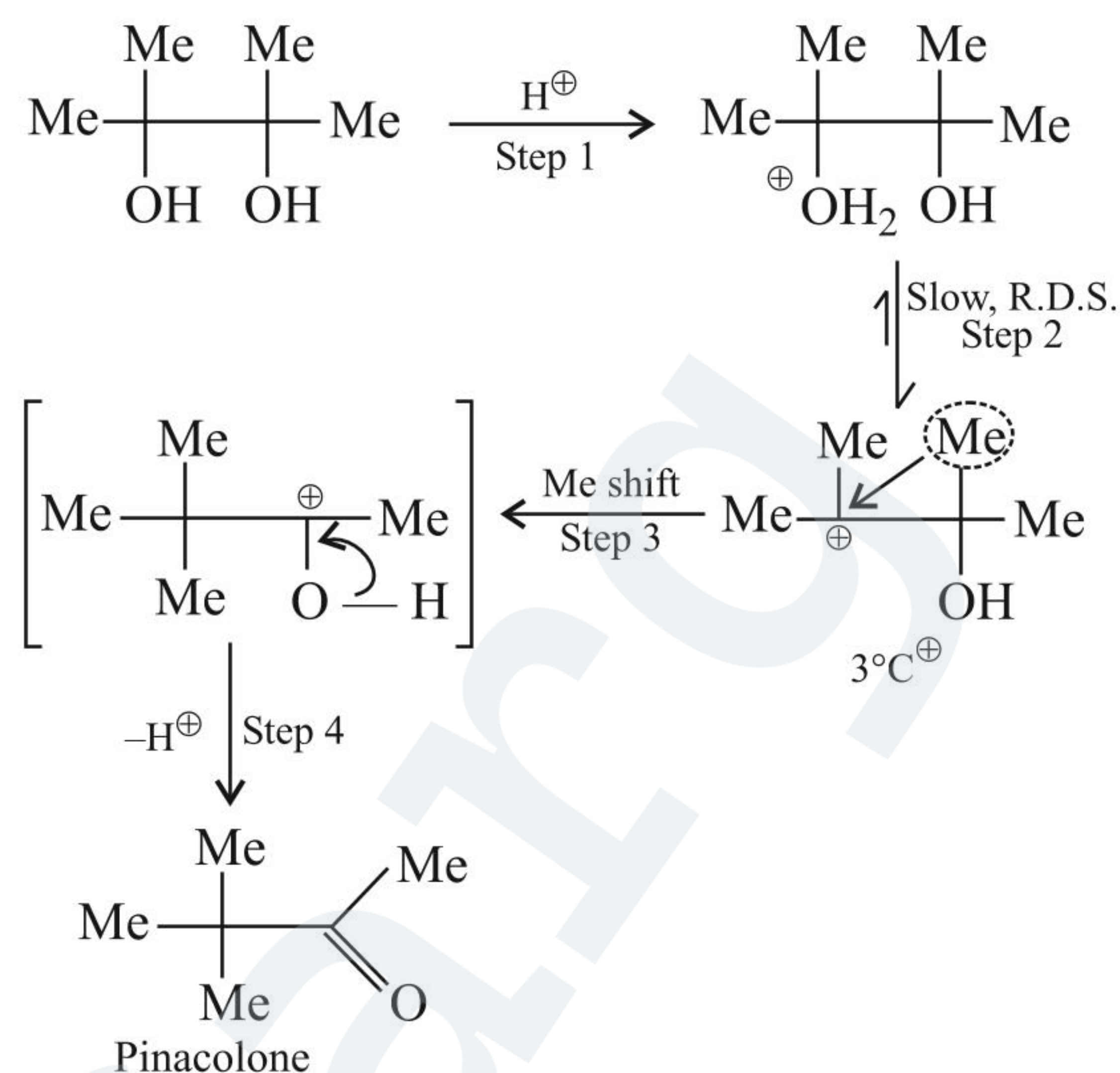


(One pair of enantiomers) + Meso form (optically inactive, due to the plane of symmetry).

4.25 PINACOL-PINACOLONE REARRANGEMENT REACTION

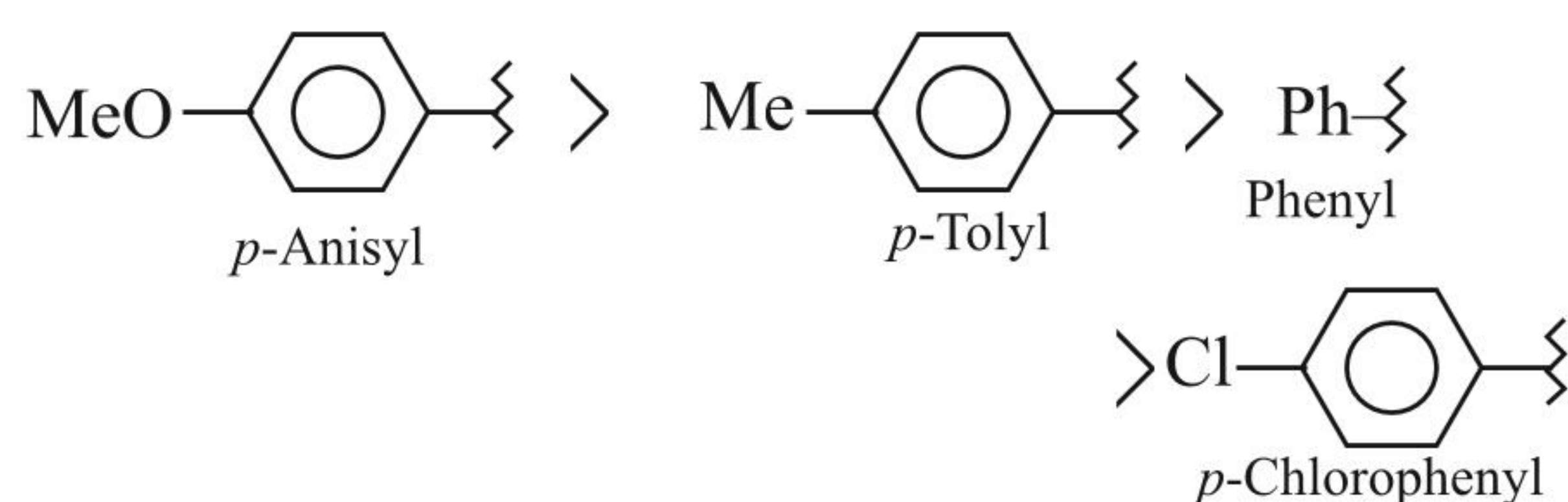
When pinacols (mostly ditertiary alcohols) are treated with mineral acids, acid chlorides, ZnCl_2 , or other electrophilic reagent, they rearrange to form ketones called pinacolones with the elimination of H_2O .

4.25.1 MECHANISM

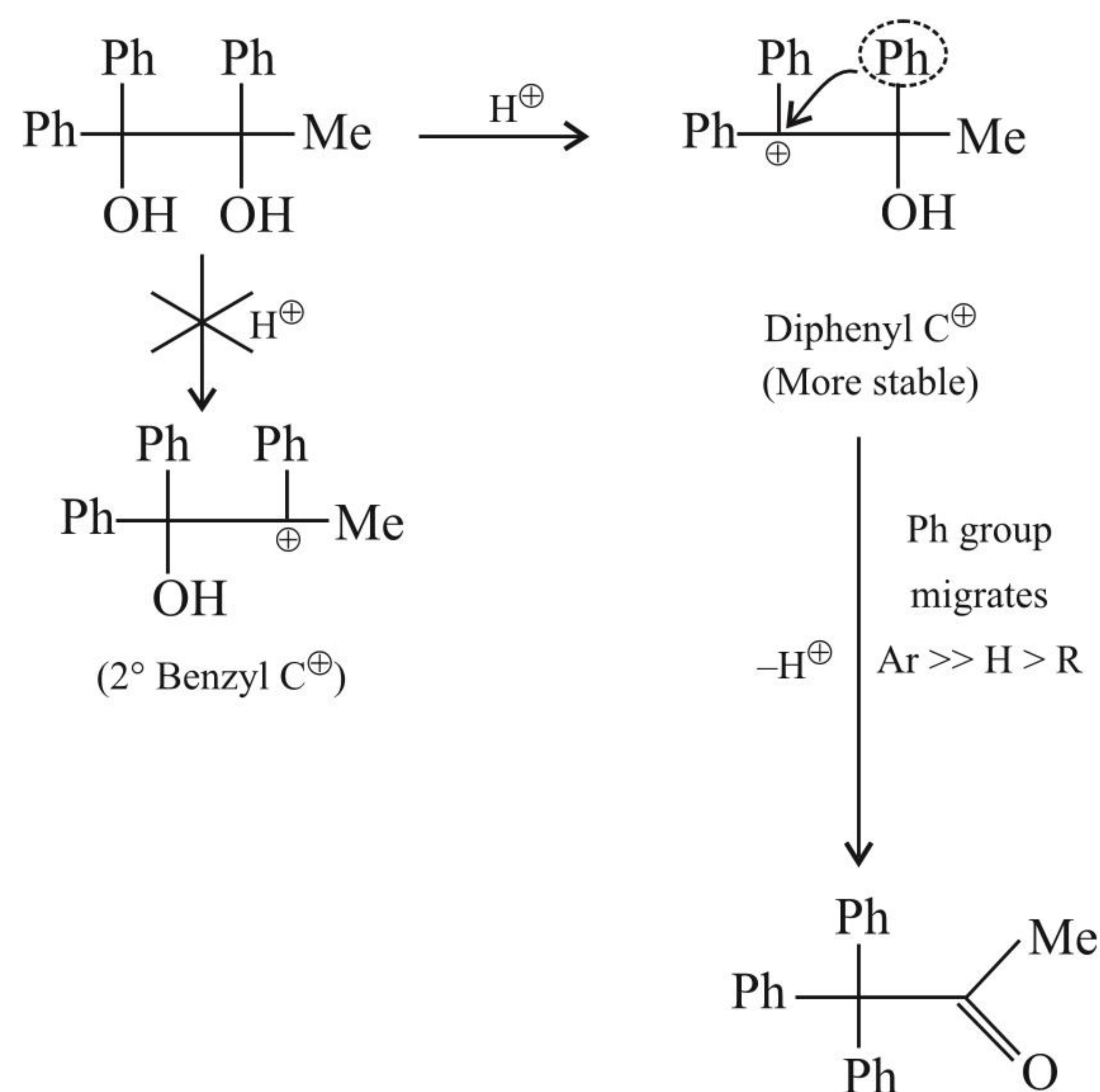


With unsymmetrical glycols, the product obtained is determined mainly by the OH that is lost as H_2O to give more stable carbocation and, thereafter, by the better migrating group.

- The order of migratory aptitudes is $\text{Ar} \gg \text{H} > \text{R}$.
- The migratory order in aryl: Ar containing more \bar{e} -donating (or more \bar{e} rich) migrates. For example,



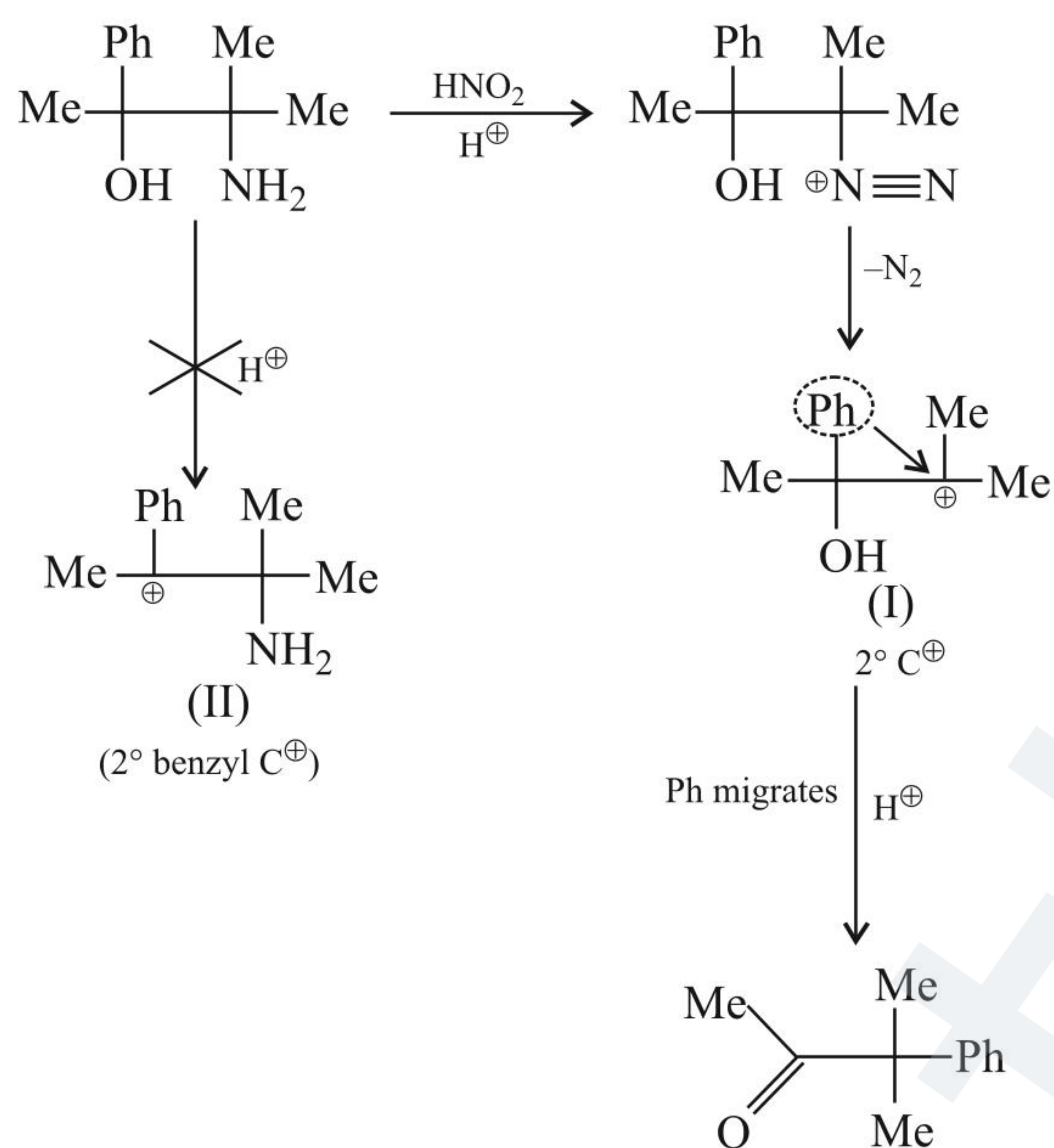
For example:



- The phenyl group is more \bar{e} rich than (Me) group, therefore (Ph) group migrates in preference to (Me) group.

- iv. The migrating group should be *trans* (anti) to the leaving (—OH) group.
- v. The (—OH) group will be lost from the C atom which would leave the most stable carbocation.
- vi. The rate determining step (R.D.S. and slow) is the formation of stable carbocation, i.e., conversion in step 2 to step 3.

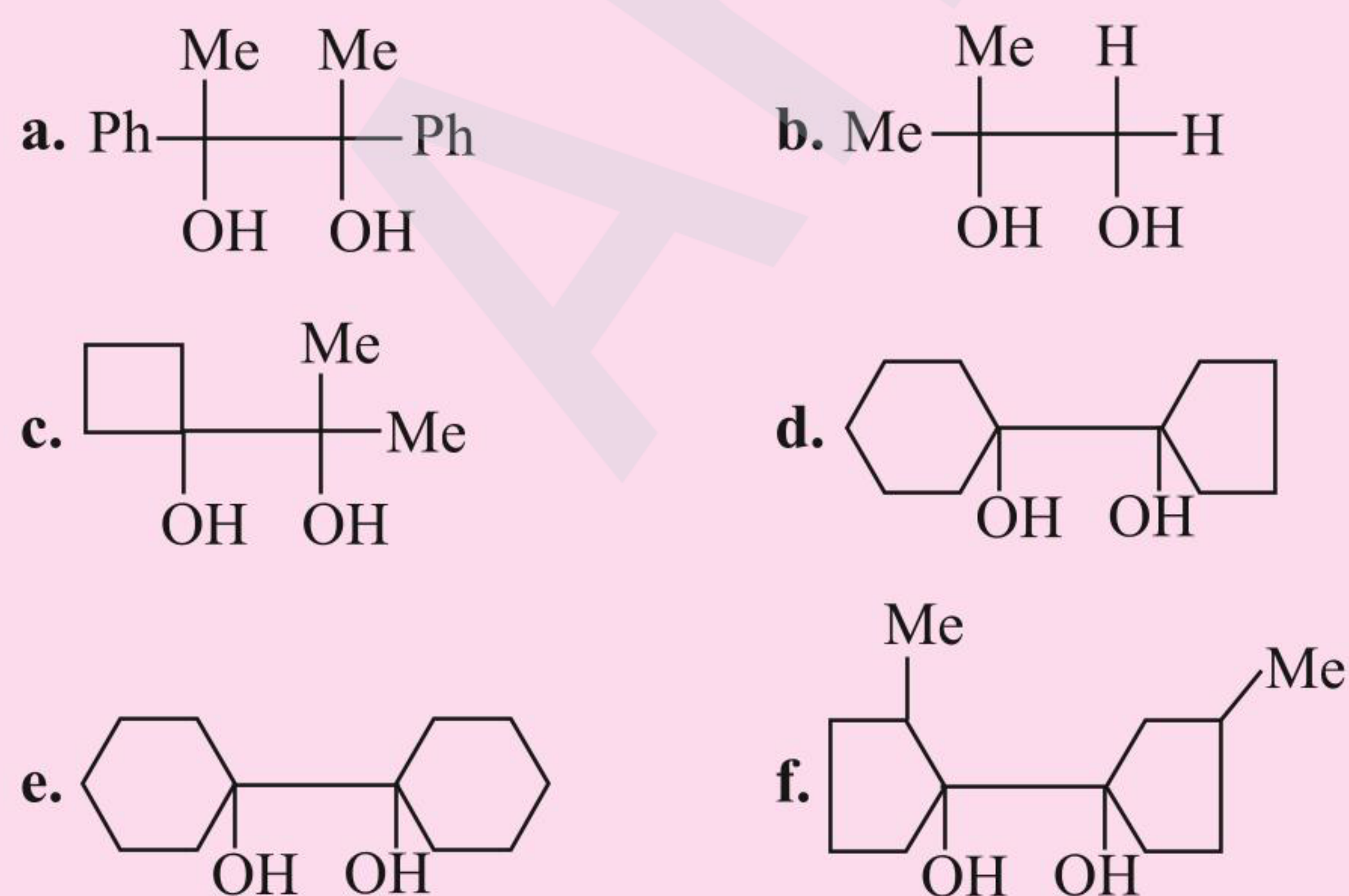
Compound containing one (OH) group and one (NH_2) group in adjacent positions, when treated with HNO_2 (or $\text{NaNO}_2 + \text{HCl}$ at $0\text{--}5^\circ\text{C}$), also undergoes this rearrangement. The carbocation formed would be on the C atom containing (—NH_2) group irrespective of the stable carbocation or not and thereafter more \bar{e} -donating group would migrate from the C-containing (OH) group, e.g.,



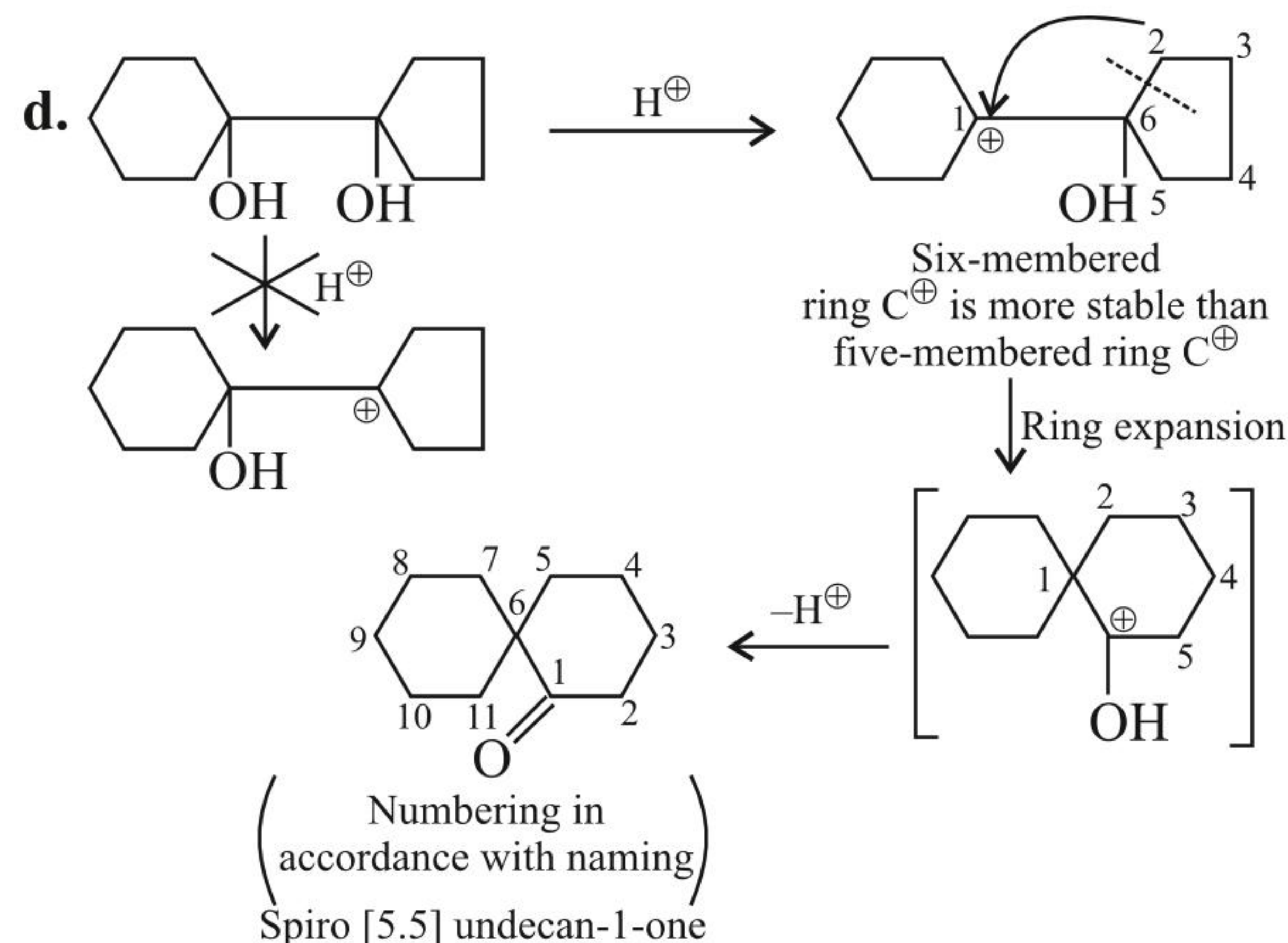
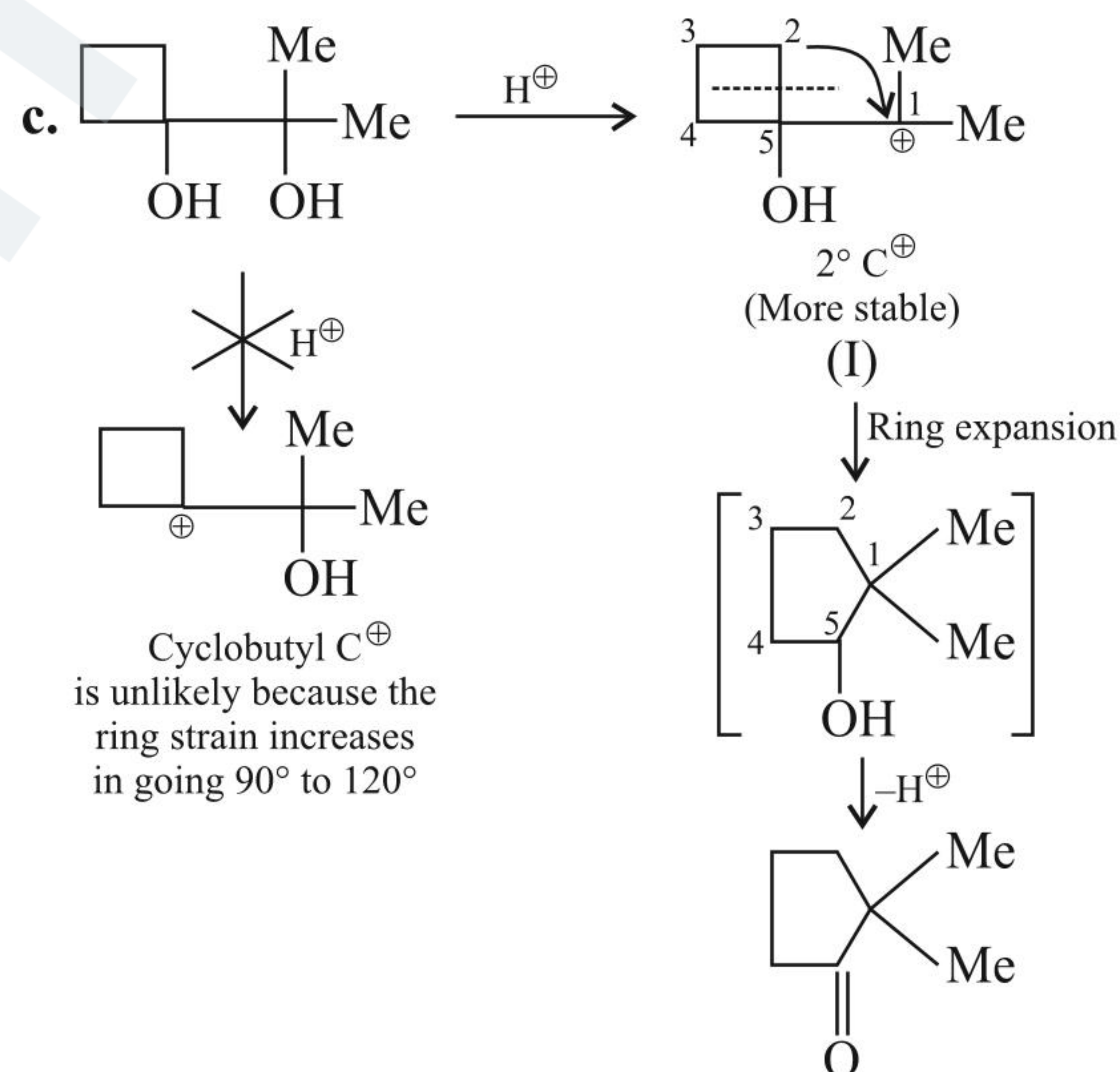
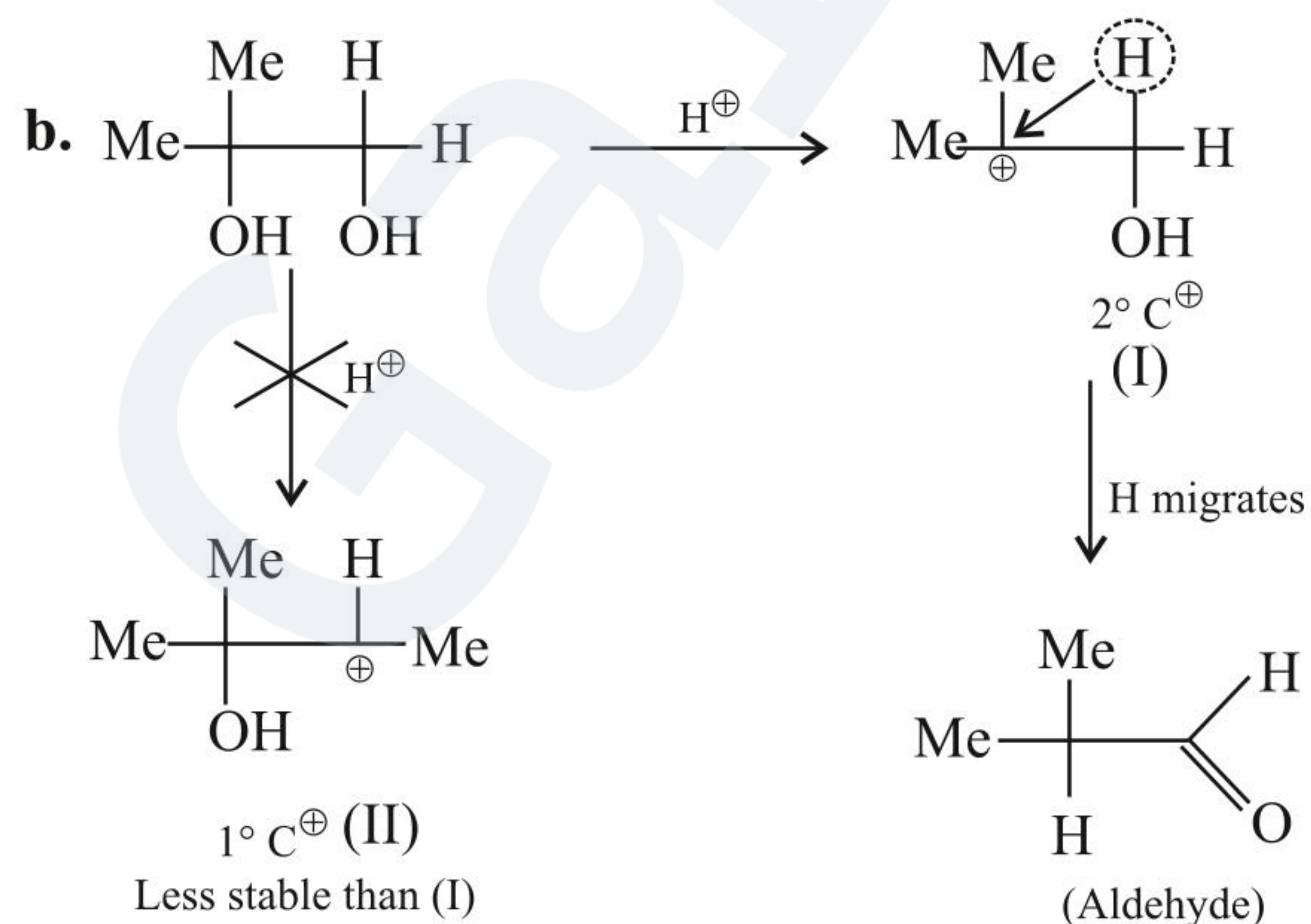
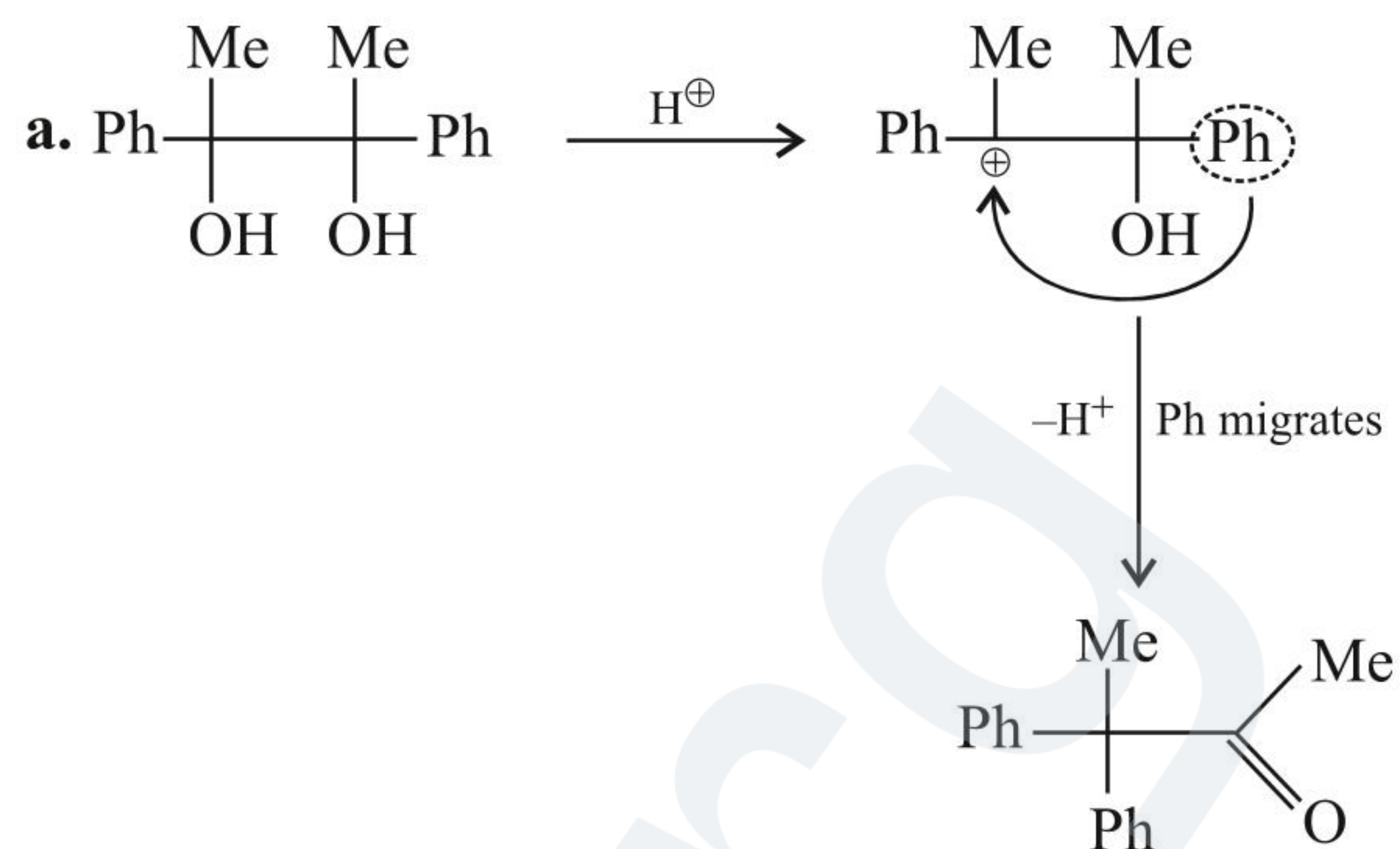
Although (II) is more stable than (I), HNO_2 first reacts with (—NH_2) group to form diazonium ion ($\text{—N}\equiv\text{N}$) which is eliminated as N_2 gas group leaving carbocation and thereafter more \bar{e} -donating groups migrate from the C-containing (OH) group.

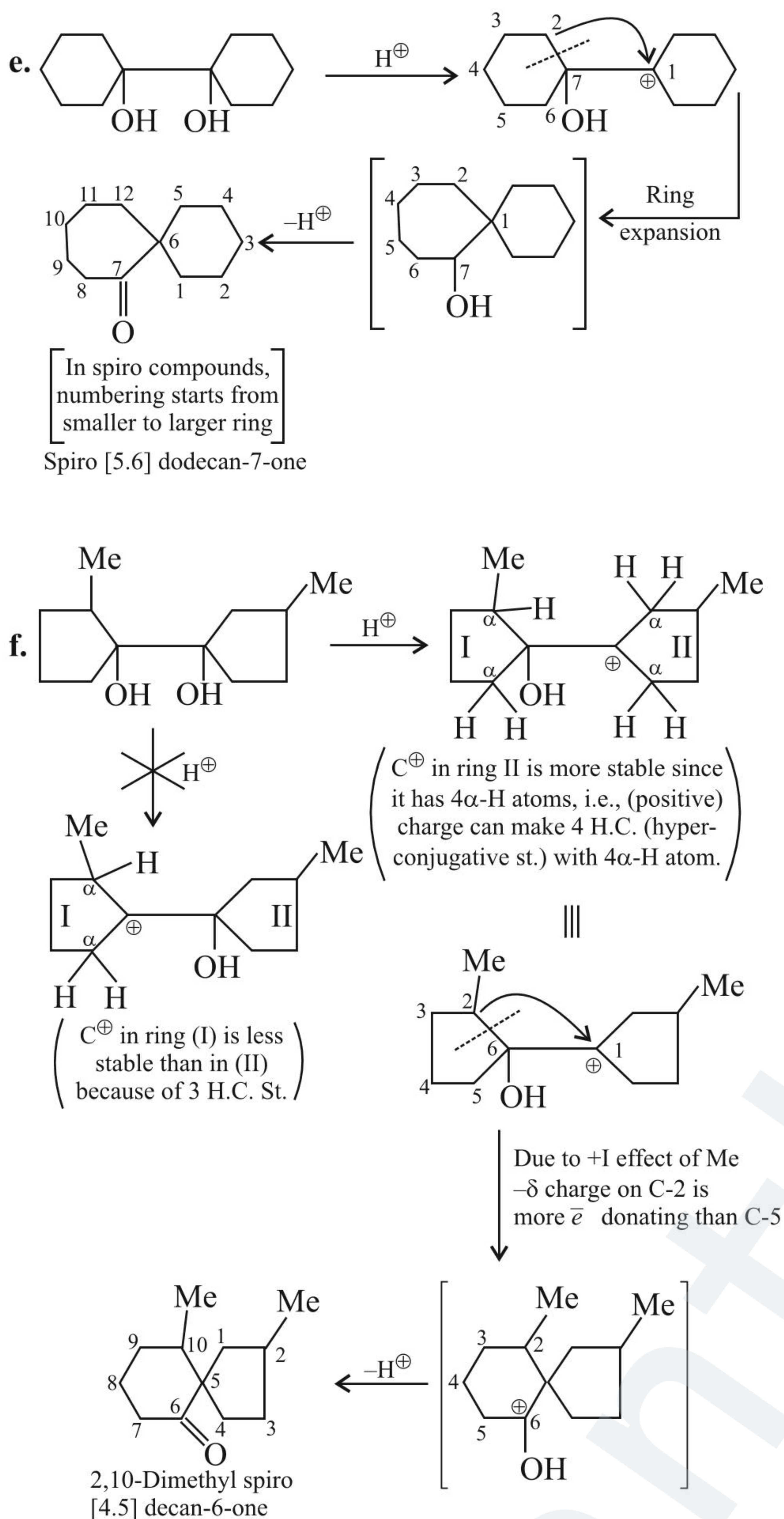
ILLUSTRATION 4.15

Give the products of the pinacol rearrangement of the following glycols in acids.



Sol.





Sol.

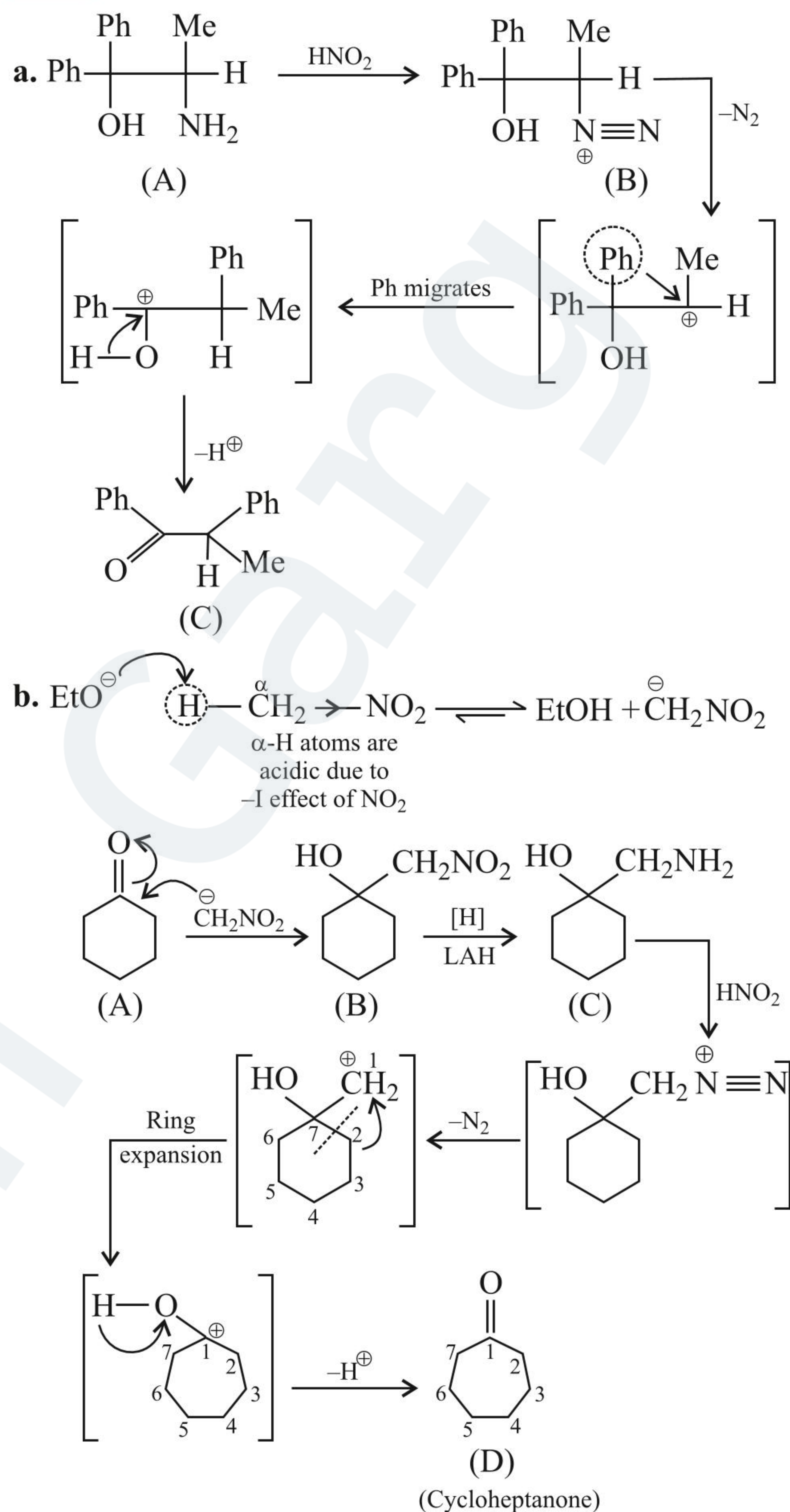
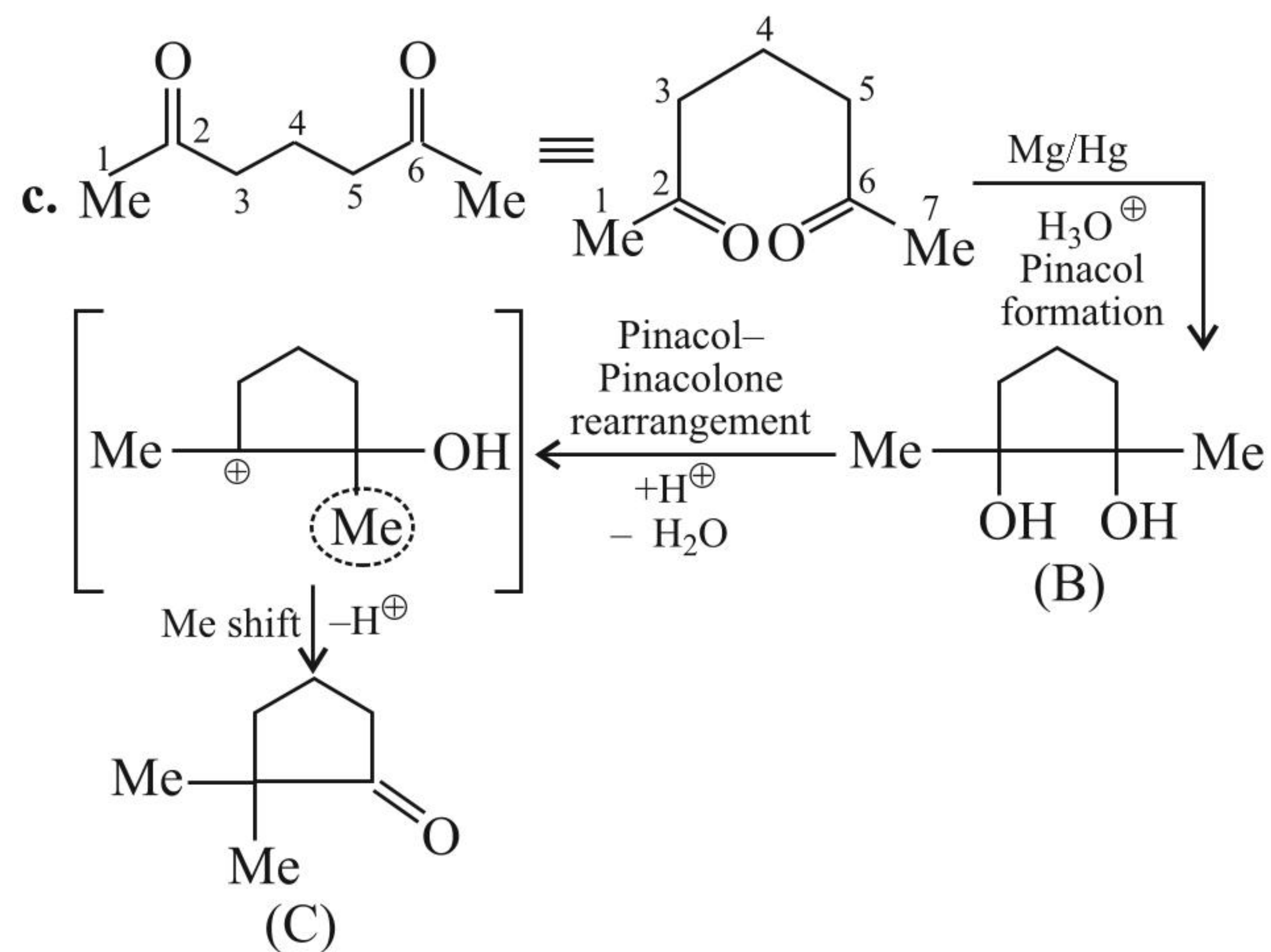
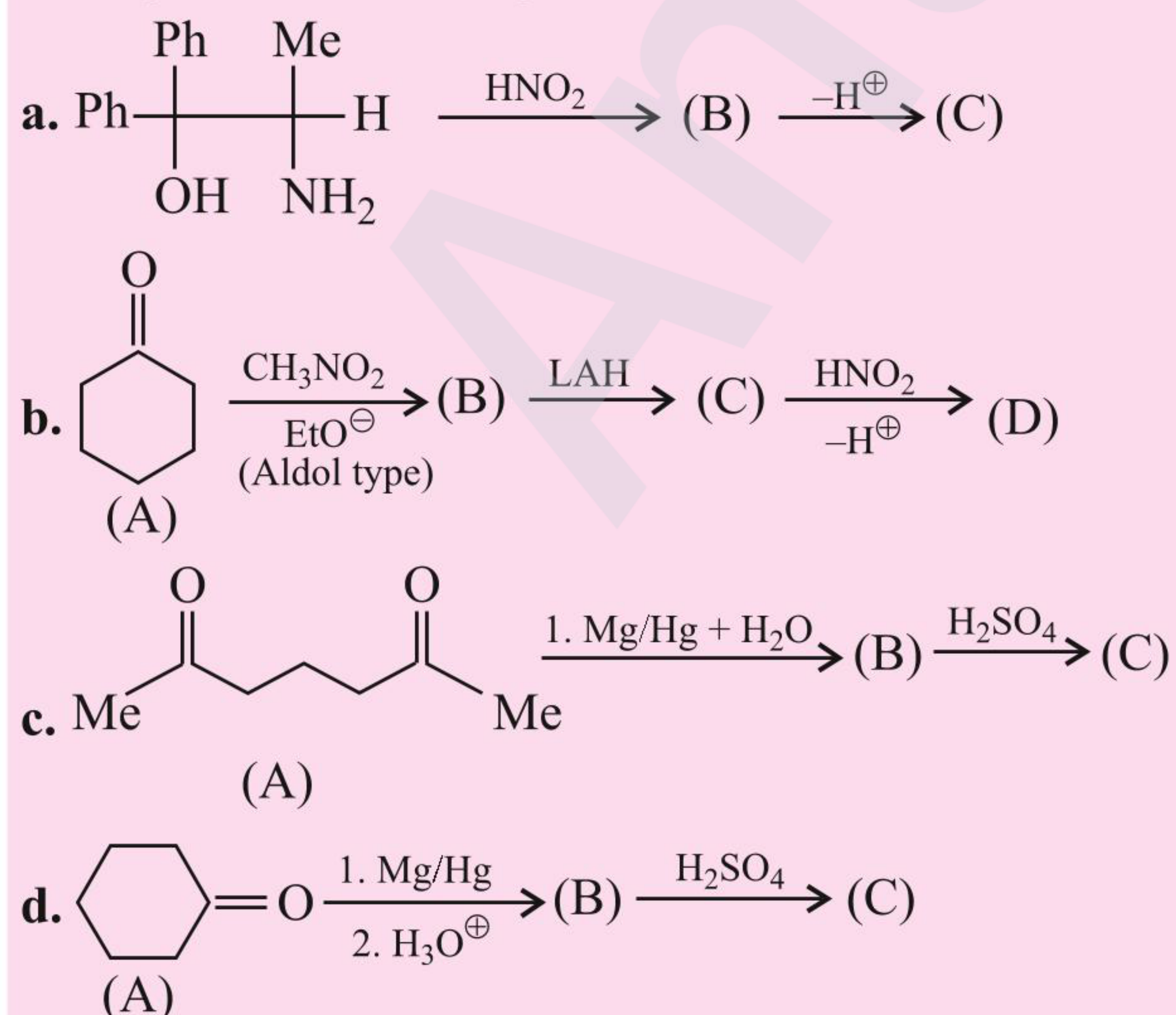


ILLUSTRATION 4.16

Complete the following reactions:



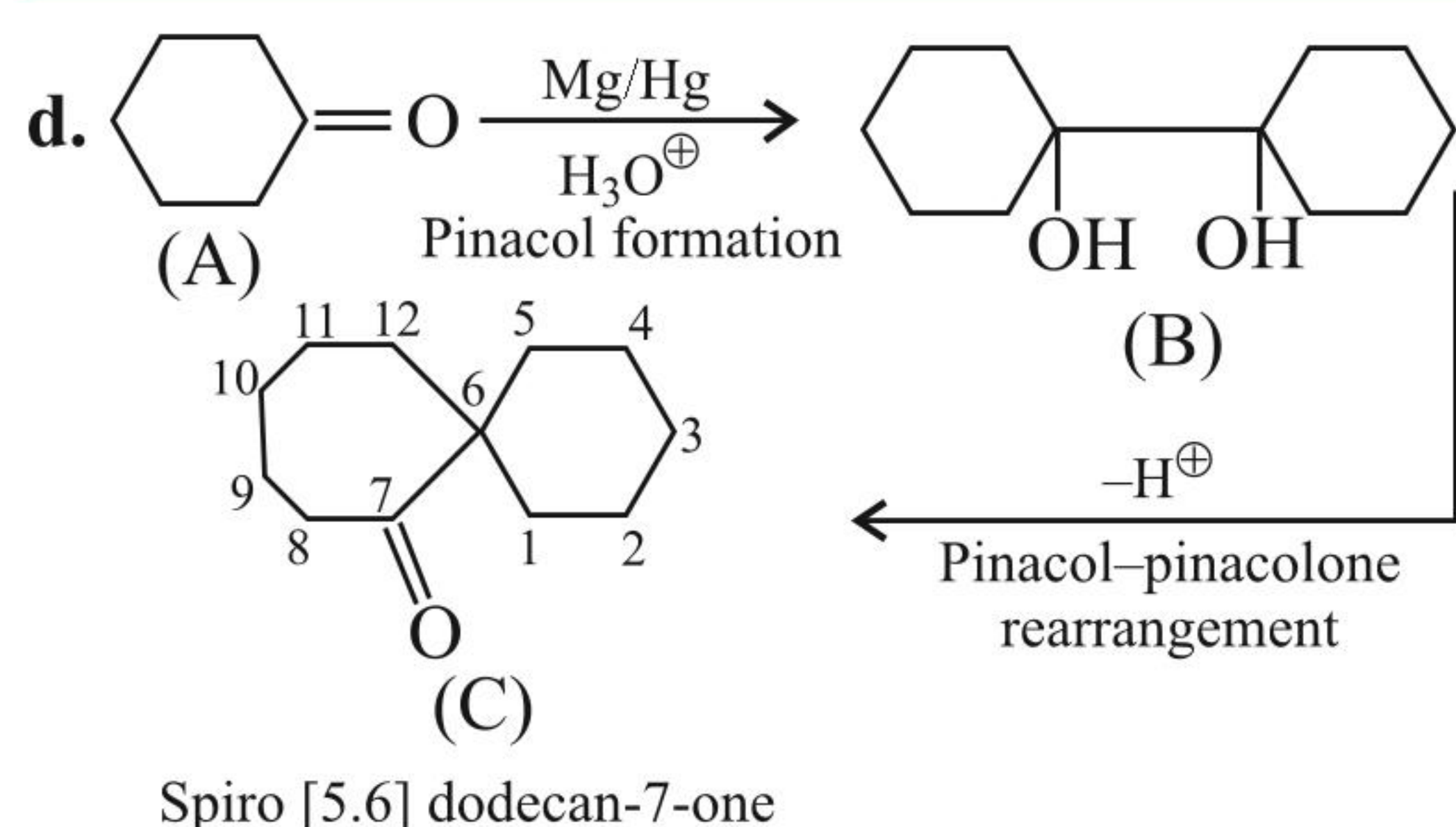
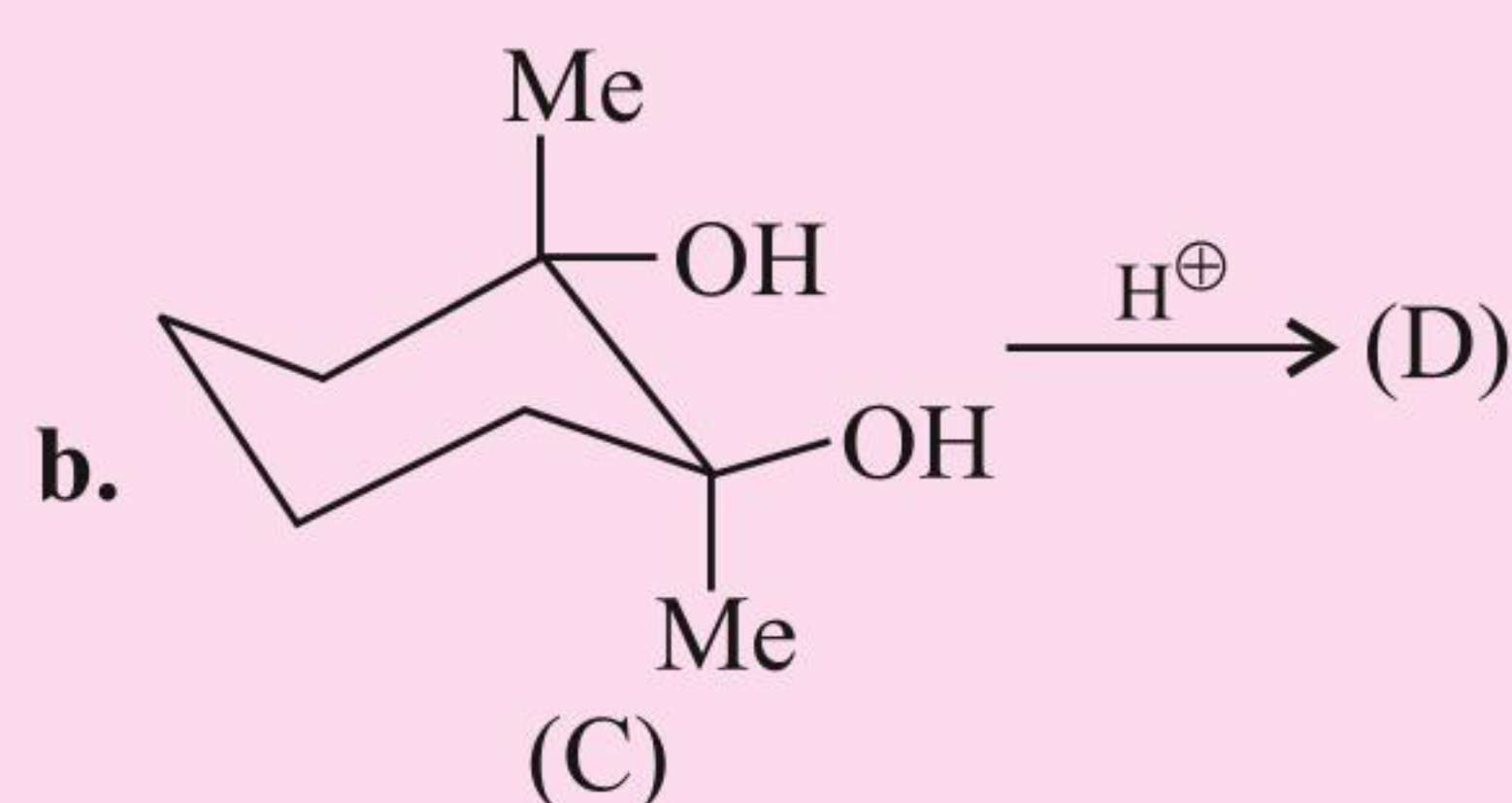
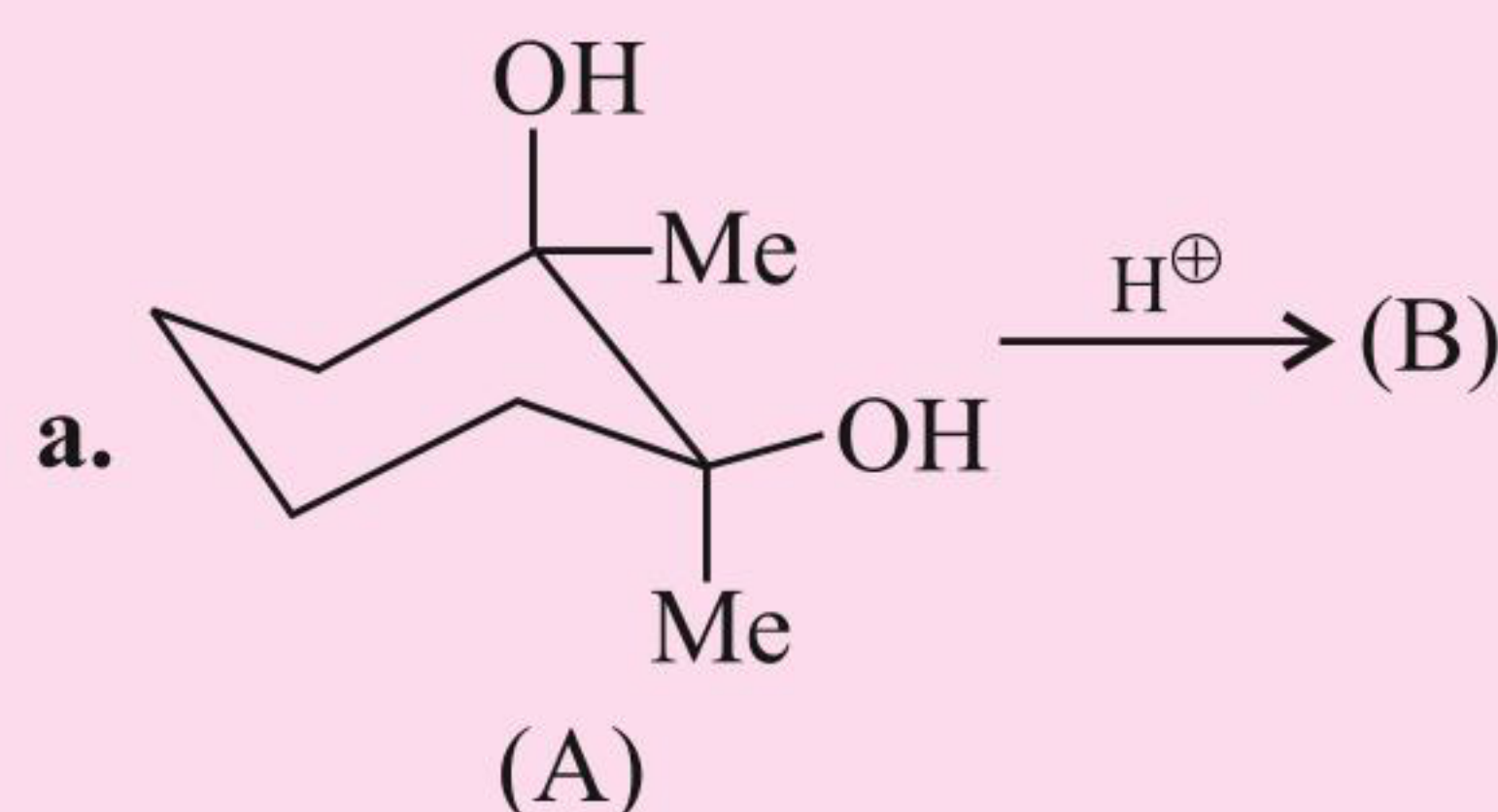


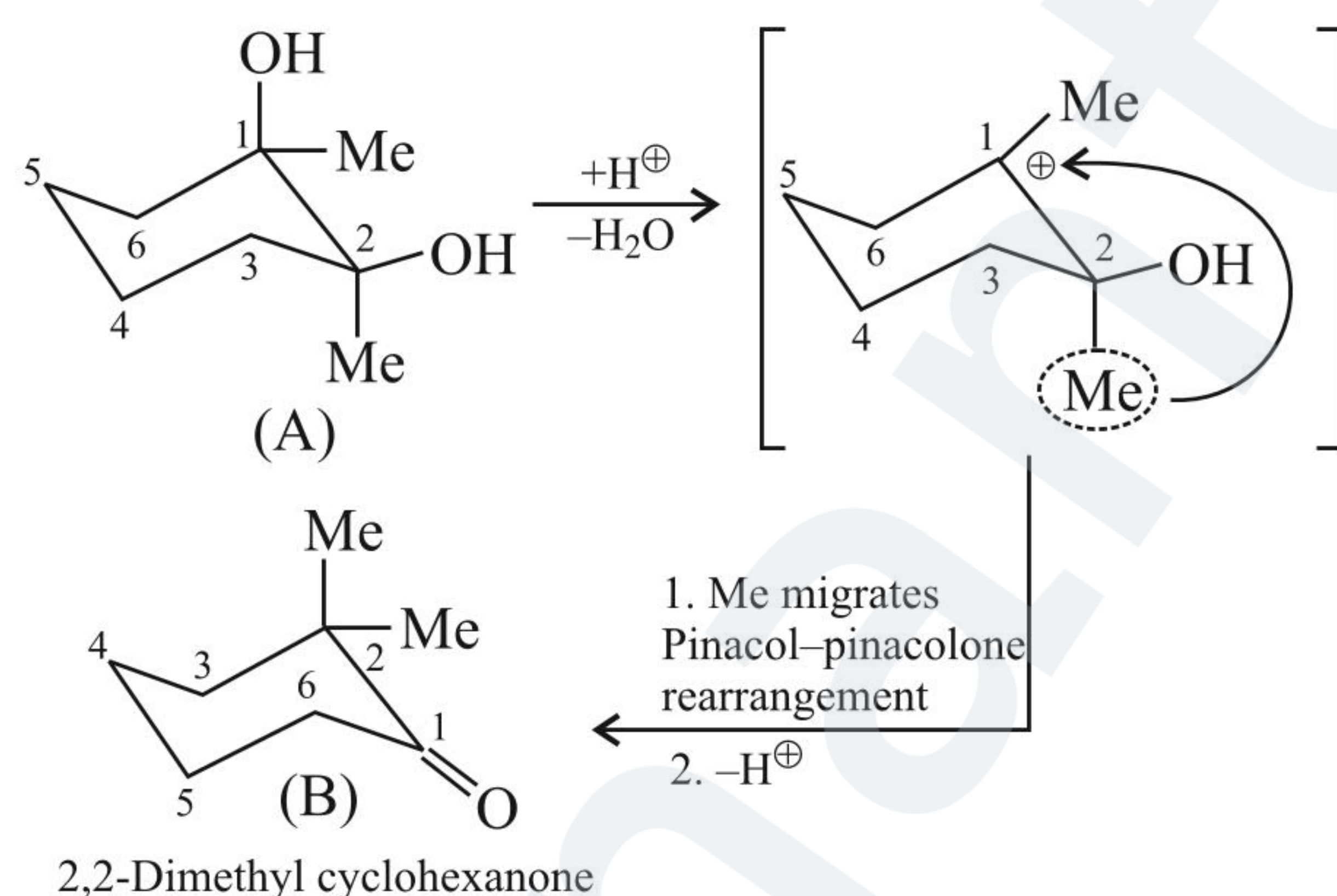
ILLUSTRATION 4.17

Give products of the following:

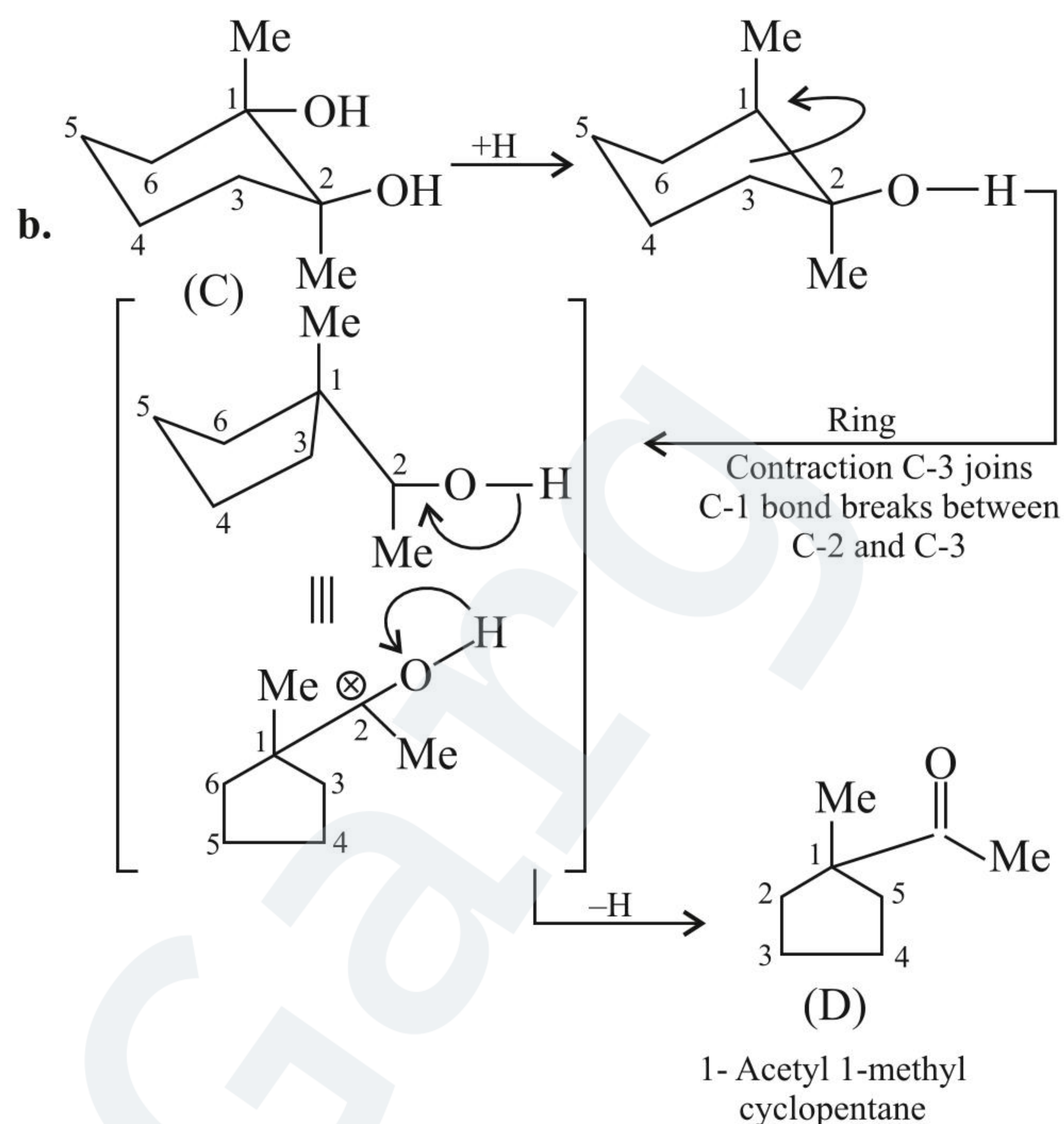


Sol.

- a. The requirement that migrating group should be *trans* to the leaving group is very important in alicyclic system.



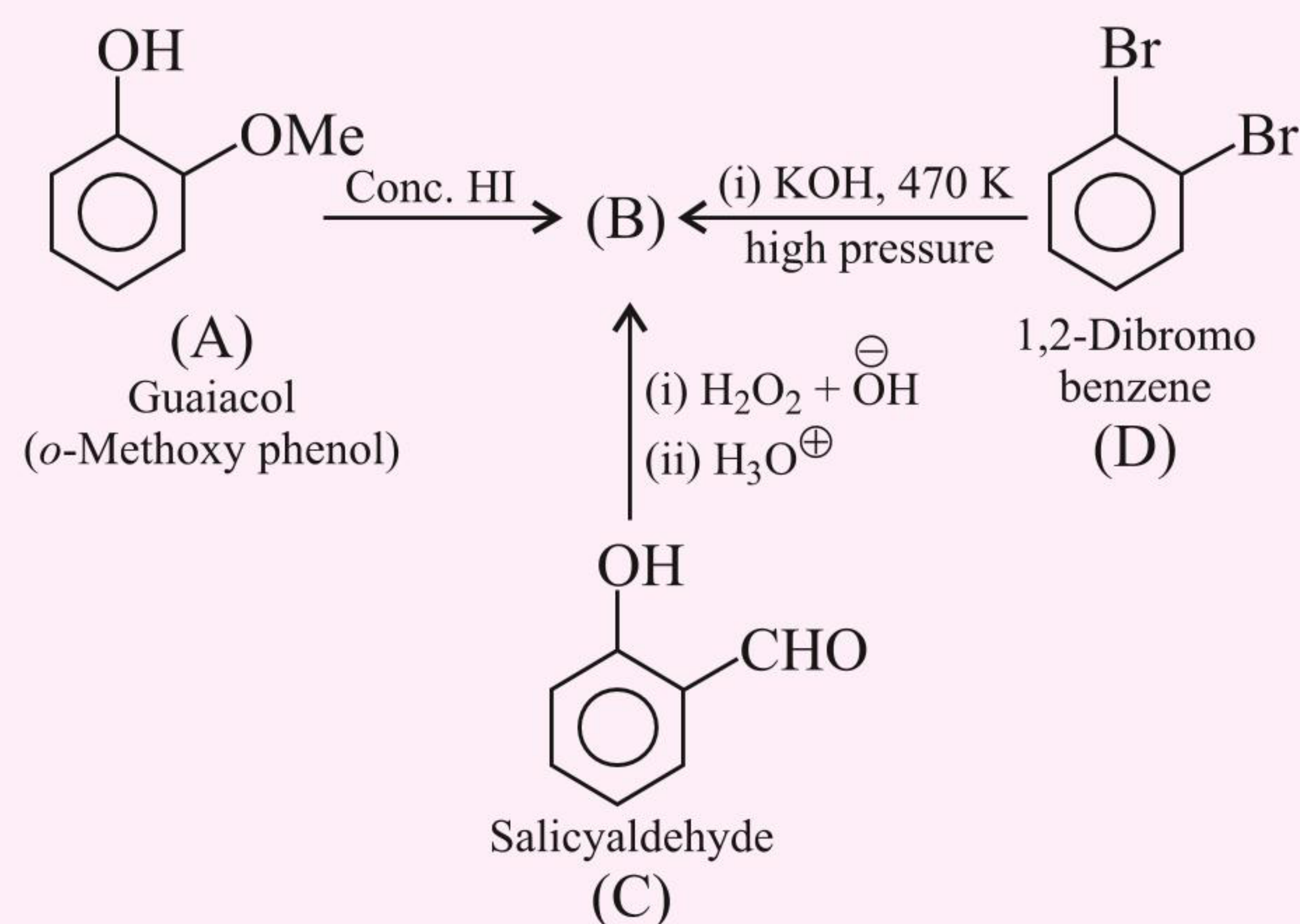
- i. Two (–OH) are in *cis* (syn) position; both (OH) are in (↑) up position; C-1 (OH) and C-2 (Me) are in *trans* (anti) position: C-1 (OH) in (↑) up position and C-2 (Me) in (↓) down position.
- ii. *trans*-Compound w.r.t. C-1 (OH) and C-2 (Me); two eliminating groups (OH) and (Me) are in *trans* position.



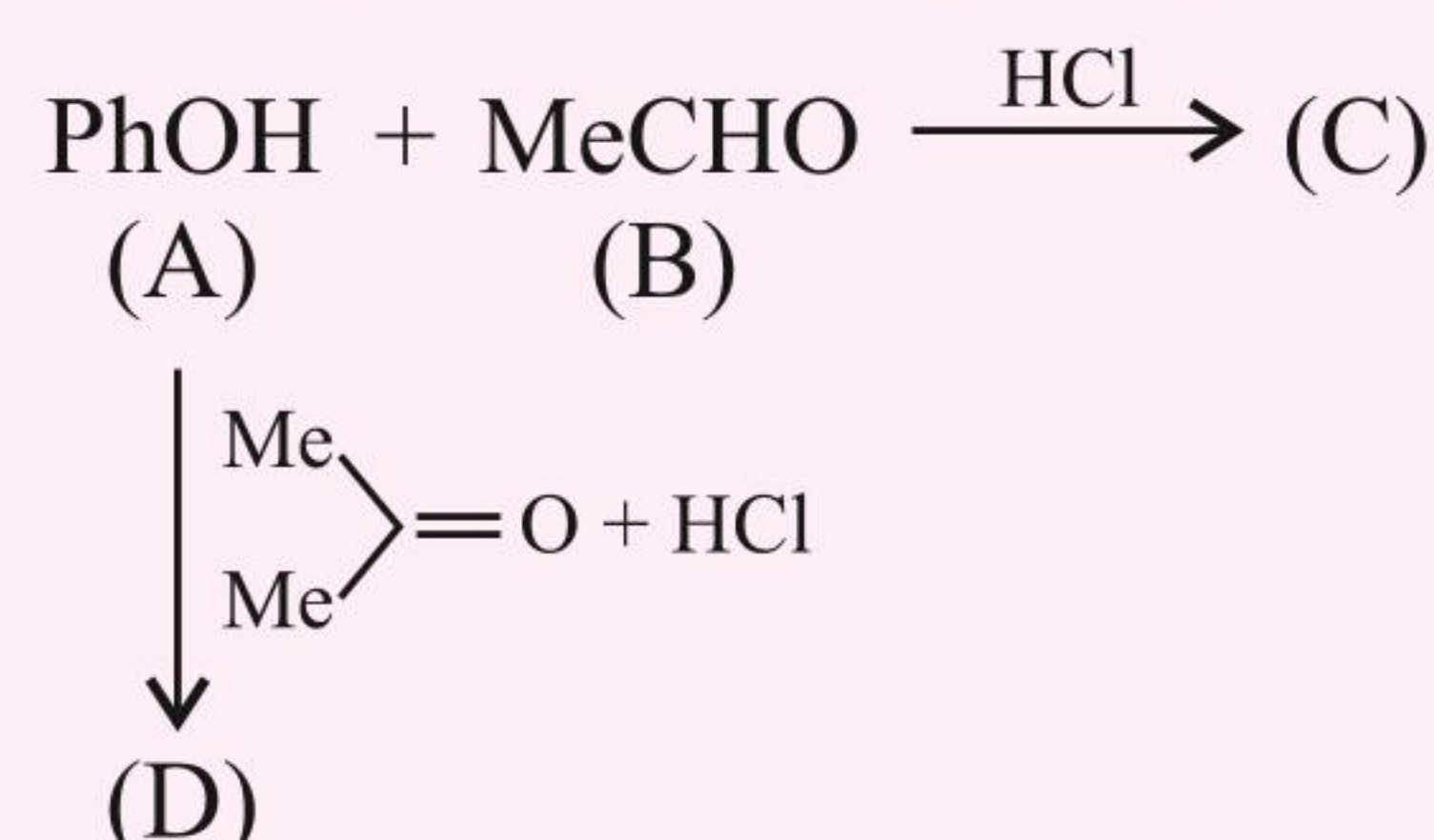
- i. Two (–OH) on C-1 and C-2 are in *trans* (anti) position, C-1 (OH) in (↓) down position but C-2 (OH) in (↑) up position; similarly, two (Me) on C-1 and C-2 are in *trans* (anti) position. C-1 (Me) is in (↑) up position and C-2 (Me) is in (↓) down position.
- ii. *cis*-compound w.r.t. C-1 (OH) and C-2 (Me); two eliminating groups (OH) and (Me) are in *cis* (syn) position.
- iii. Pinacol-pinacolone rearrangement does not occur, instead dehydration takes by the the ring contraction to give cyclopentyl derivative.

CONCEPT APPLICATION EXERCISE 4.1

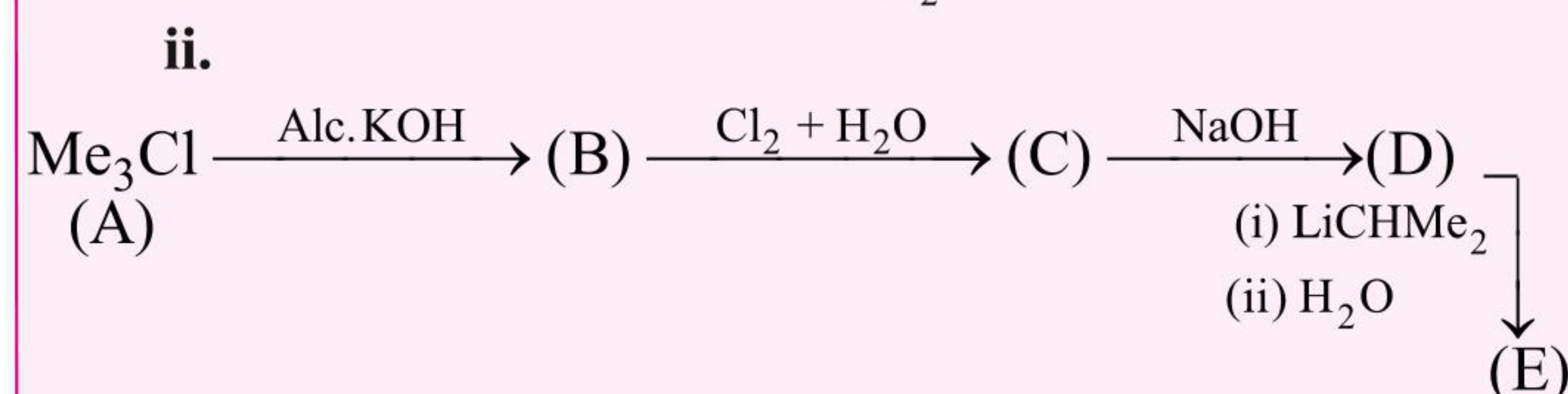
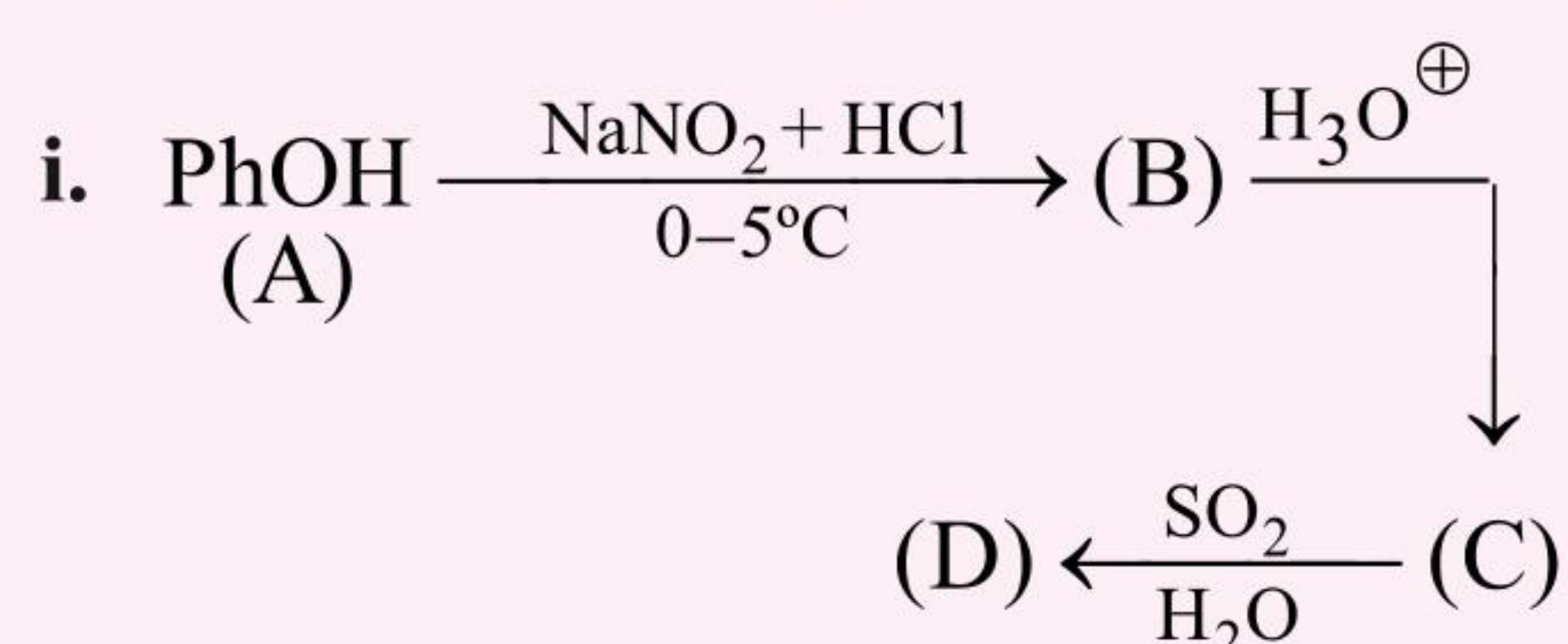
1. Identify the following compounds:



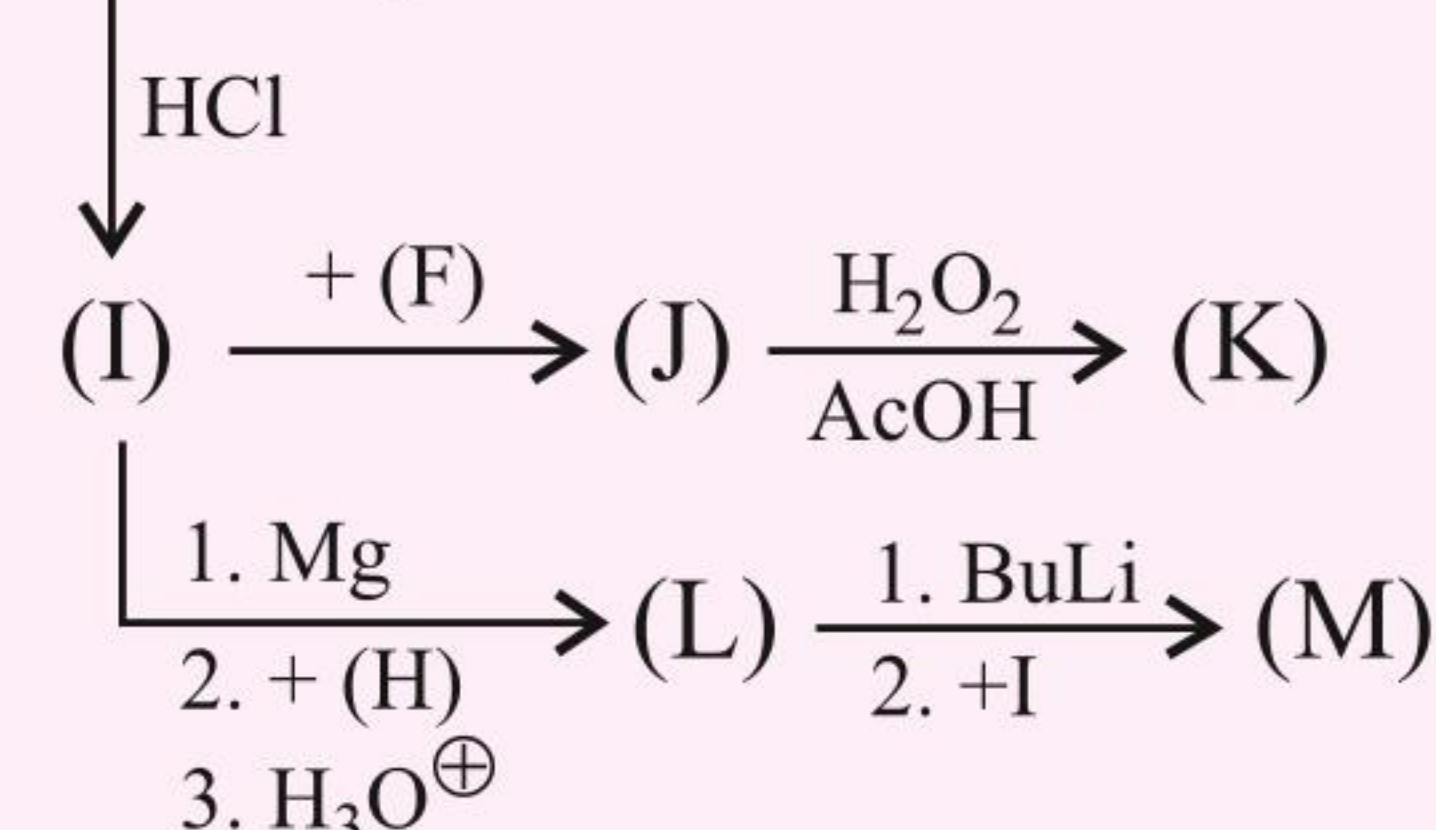
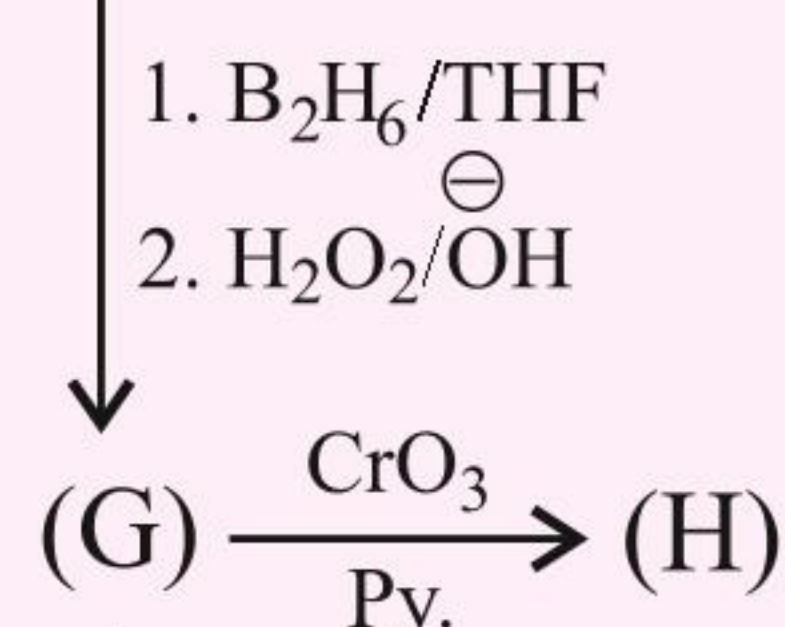
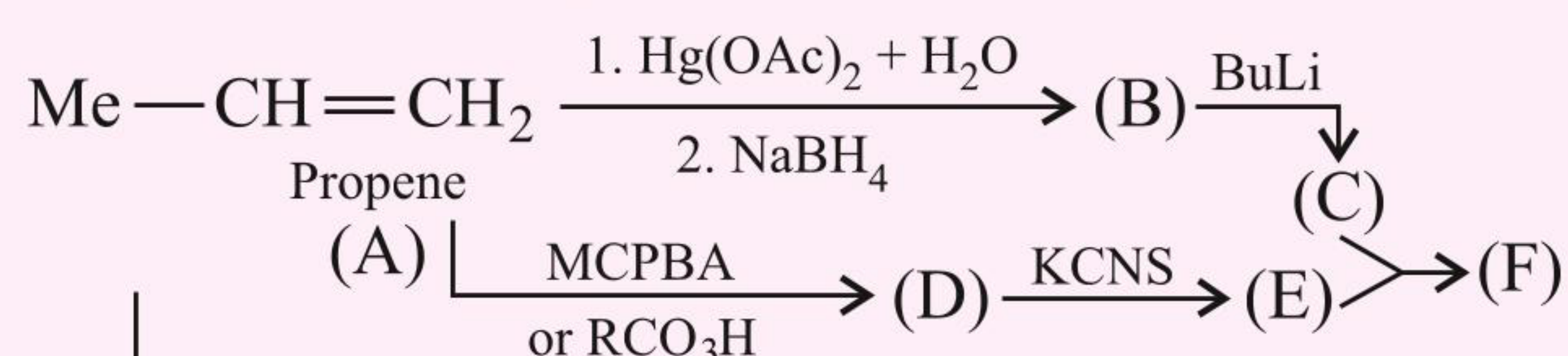
2. Identify the following compounds:



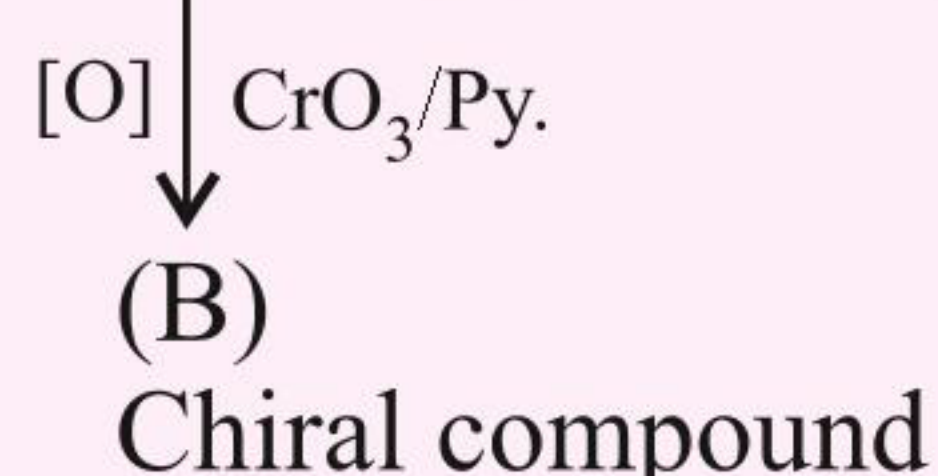
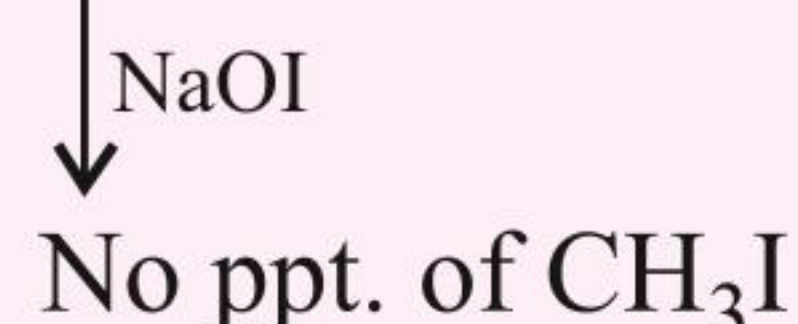
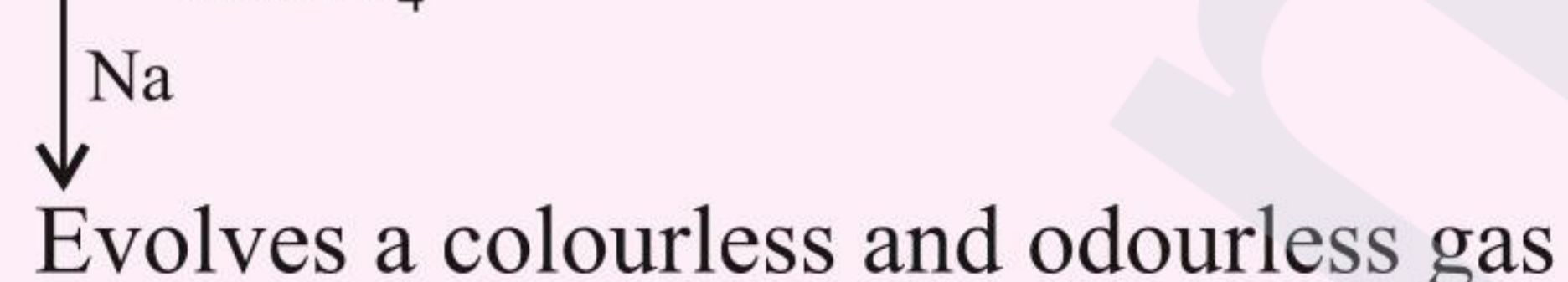
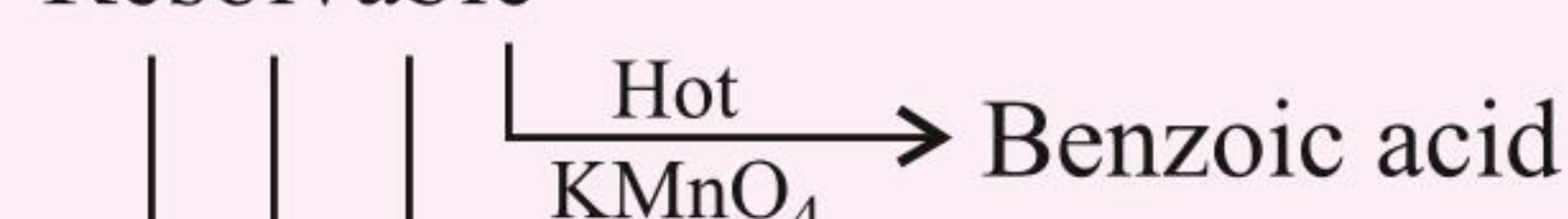
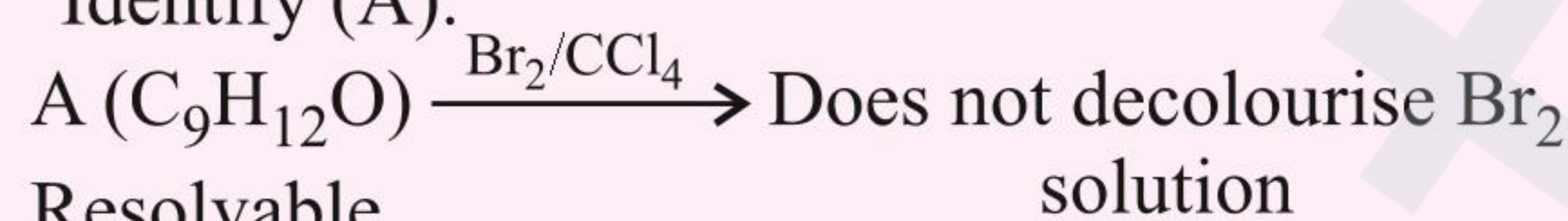
3. Identify the following compounds:



4. Identify the following compounds:



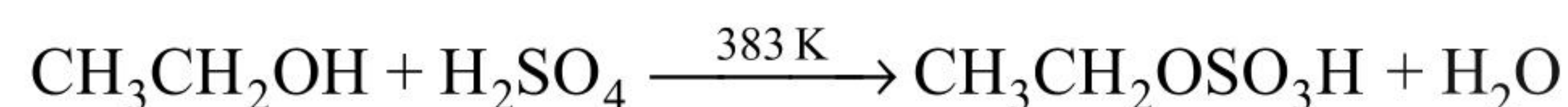
5. Identify (A).



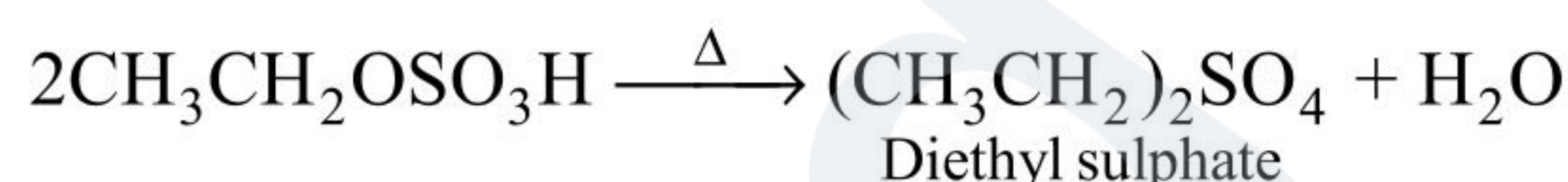
6. C_7H_{14} (A) decolourises Br_2 in CCl_4 and reacts with $\text{Hg}(\text{OAc})_2$ in THF H_2O followed by reduction with NaBH_4 to produce a resolvable compound (B). (A) undergoes reductive ozonolysis to give the same compound (C) obtained by oxidation of hexan-3-ol with KMnO_4 . Identify (A), (B), and (C).

a. Reaction of alcohol with conc. H_2SO_4 under different conditions:

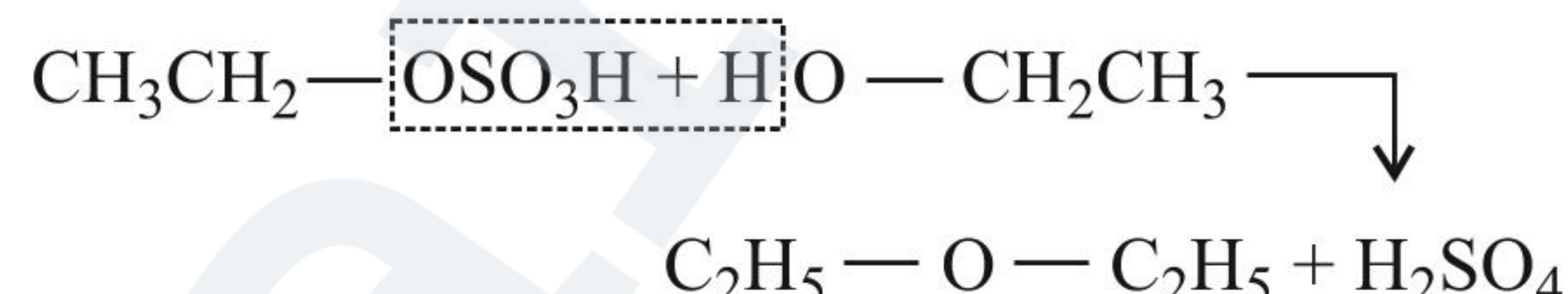
i. At 383 K (110°C), alkyl hydrogen sulphate is formed,



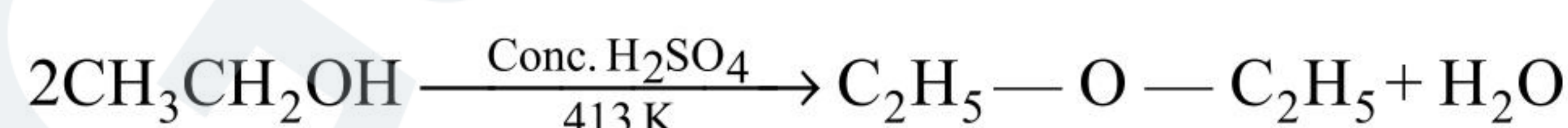
ii. When ethyl hydrogen sulphate is further heated under reduced pressure, it gives diethyl sulphate.



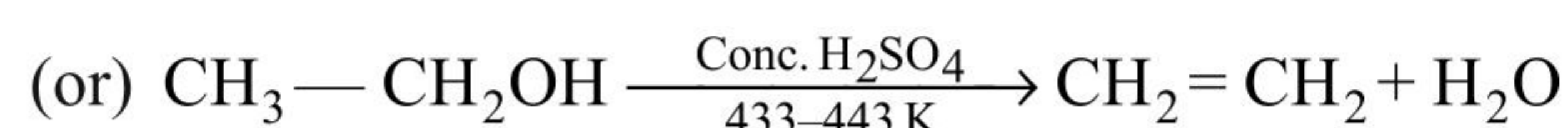
iii. When ethyl hydrogen sulphate is heated to 413 K (140°C) in the presence of excess of alcohol, diethyl ether is formed.



The reaction of ethyl alcohol with conc. H_2SO_4 at 413 K (140°C) may be directly written as:

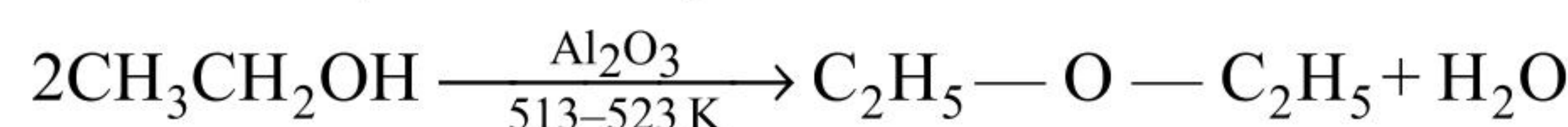


iv. When ethyl hydrogen sulphate is heated to 433–443 K ($160-170^\circ\text{C}$) in the presence of excess of conc. H_2SO_4 , ethylene is produced, i.e., dehydrogenation of ethyl alcohol takes place.

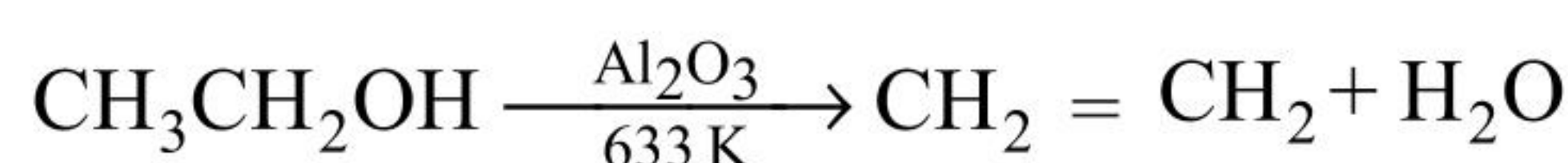


b. Reaction with heated alumina (Al_2O_3):

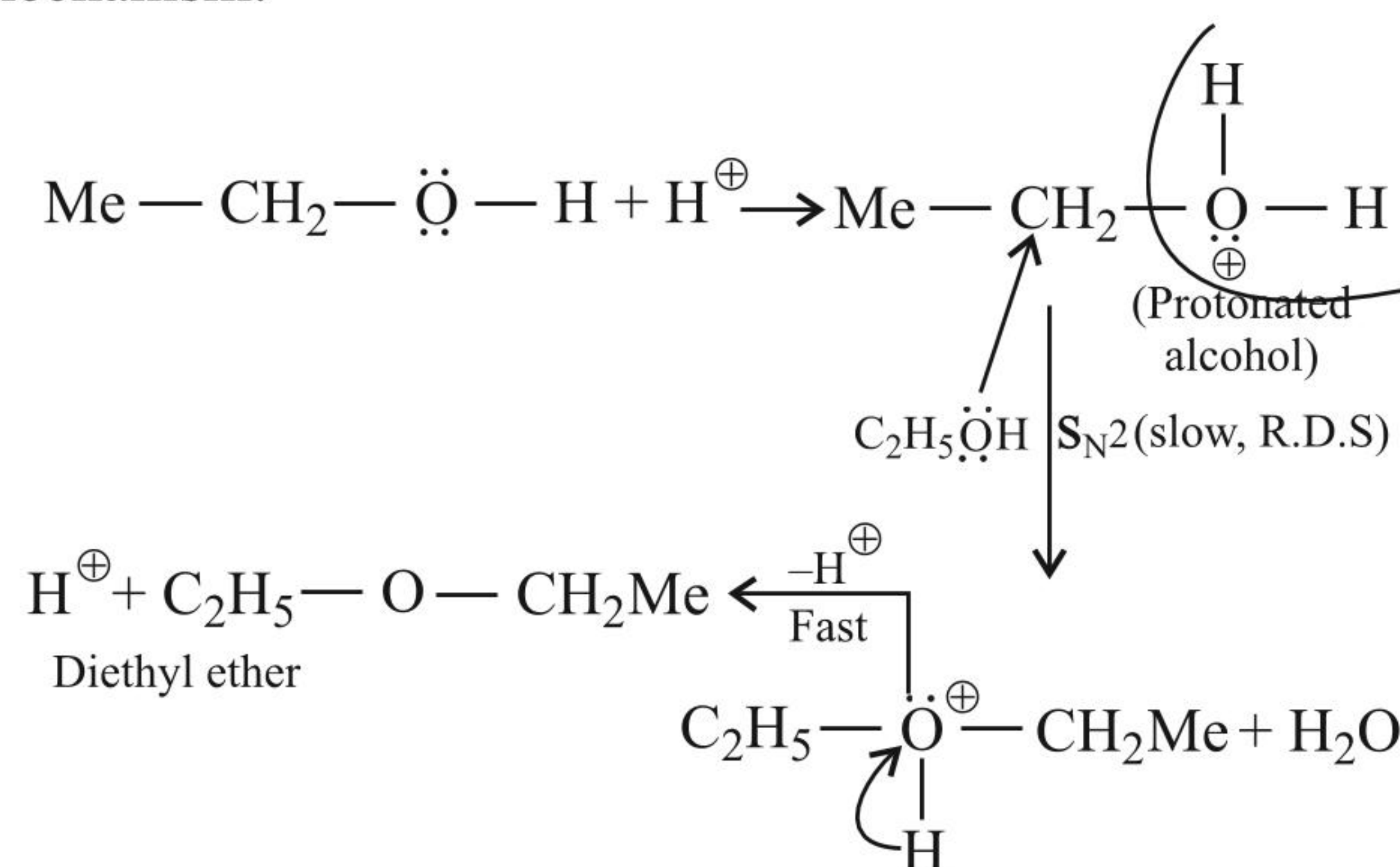
i. At 513–523 K ($240-250^\circ\text{C}$):



ii. At 633 K (380°C):



c. Mechanism: The formation of ether takes place by $\text{S}_\text{N}2$ mechanism:



This method is suitable for the preparation of ethers having 1° alkyl groups only. The alkyl group should be unhindered and reaction should be carried out at low temperature, otherwise alkene would be formed. When alcohol is 2° or 3° , the reaction would proceed via $\text{S}_\text{N}1$ mechanism.

4.26 PREPARATION OF ETHERS (ETHERIFICATION)

4.26.1 DEHYDRATION OF ALCOHOLS UNDER DIFFERENT CONDITIONS

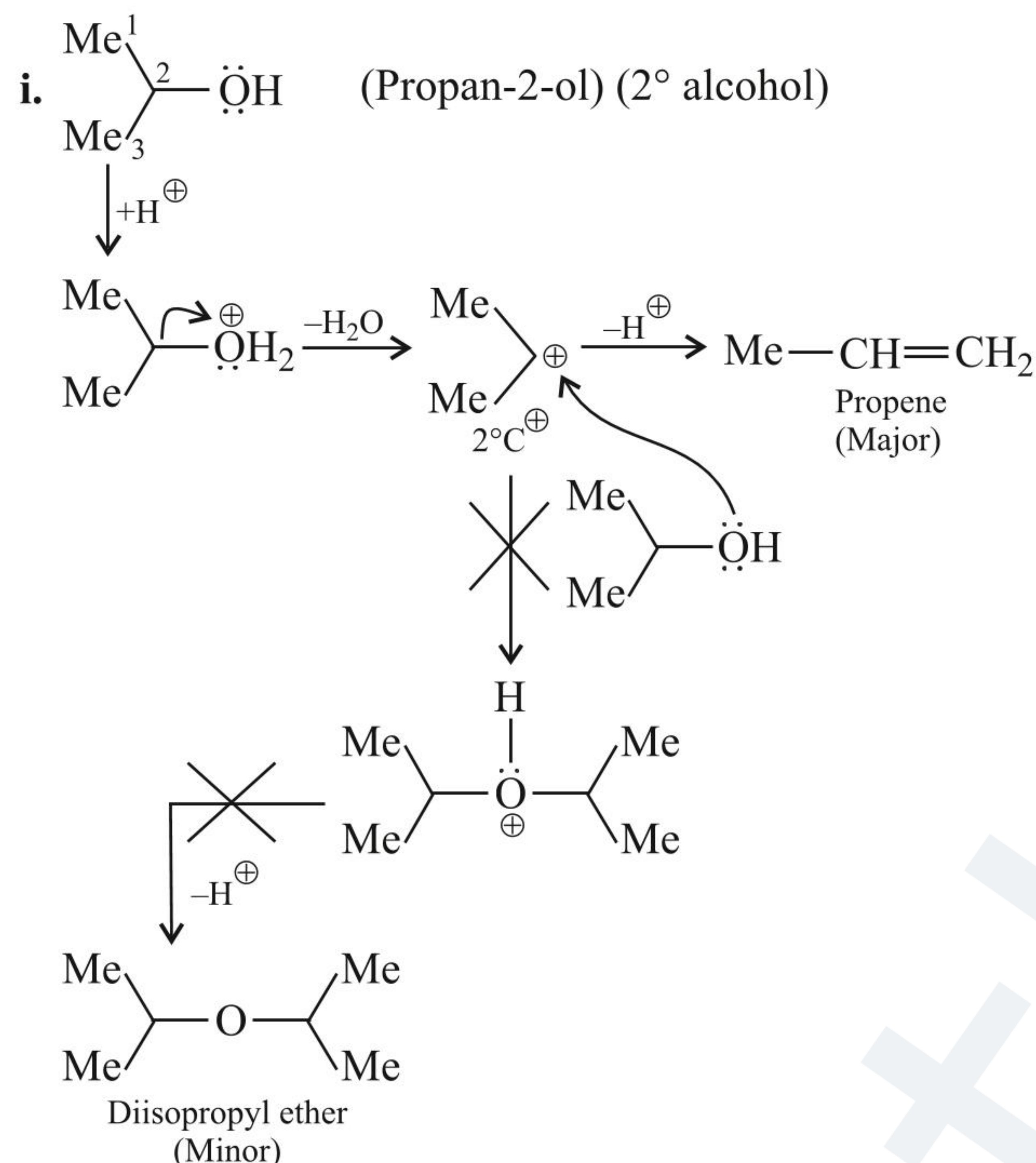
Dehydration of alcohols under different reaction conditions gives different products:

In the dehydration of 2° or 3° alcohols, elimination completely overcomes substitution and alkenes are formed.

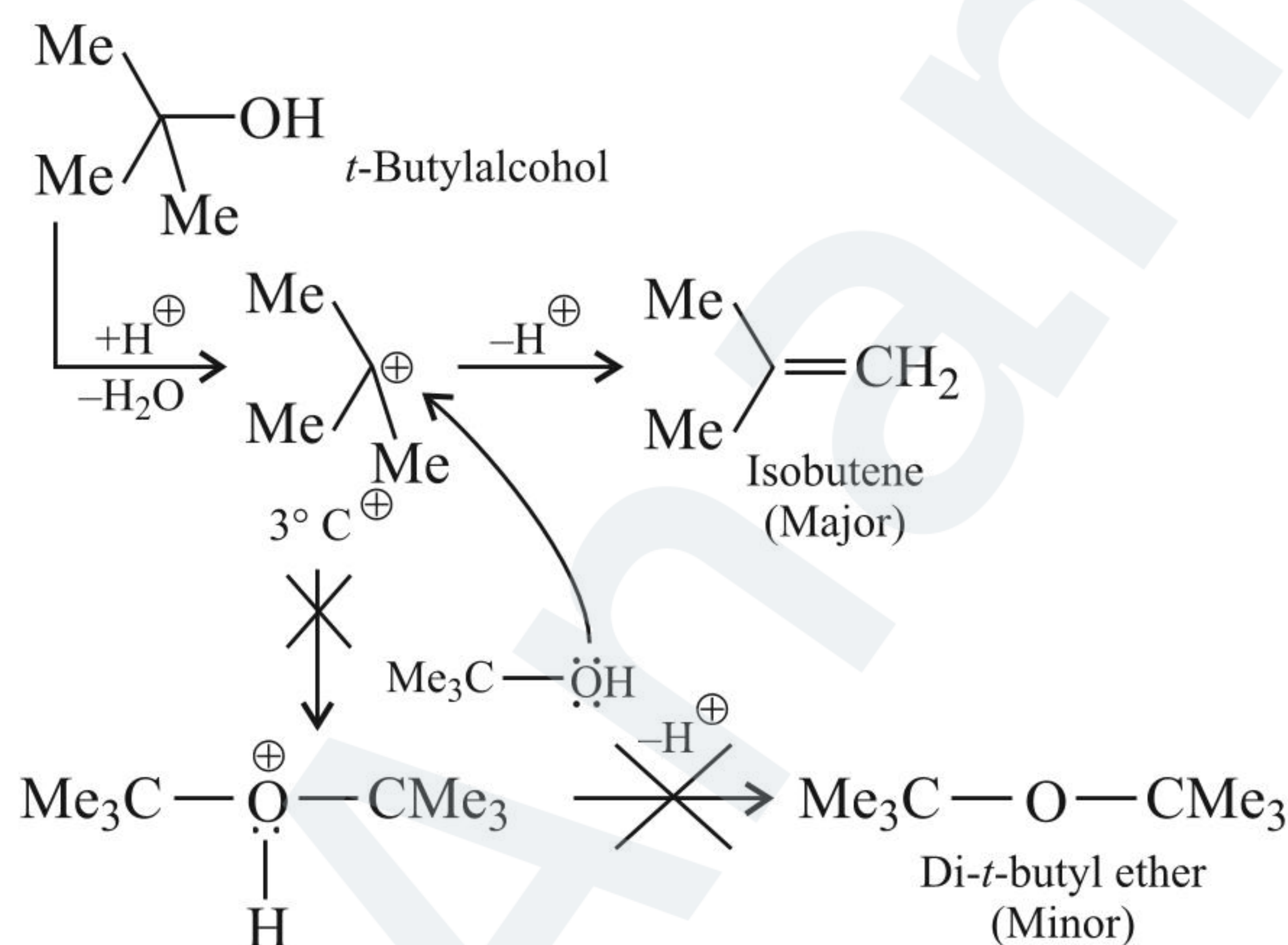
Ethyl methyl ether (C₂H₅—O—CH₃) cannot be prepared by bimolecular dehydration of alcohols.

d. Bimolecular dehydration of 2° and 3° alcohol:

Due to steric hindrance in 2° and 3° alcohol, nucleophilic attack by the alcohol molecule on protonated alcohol does not occur but protonated 2° and 3° alcohol lose a molecule of H₂O to form stable 2° and 3° C⁺, which form alkene after the loss of H⁺. For example,



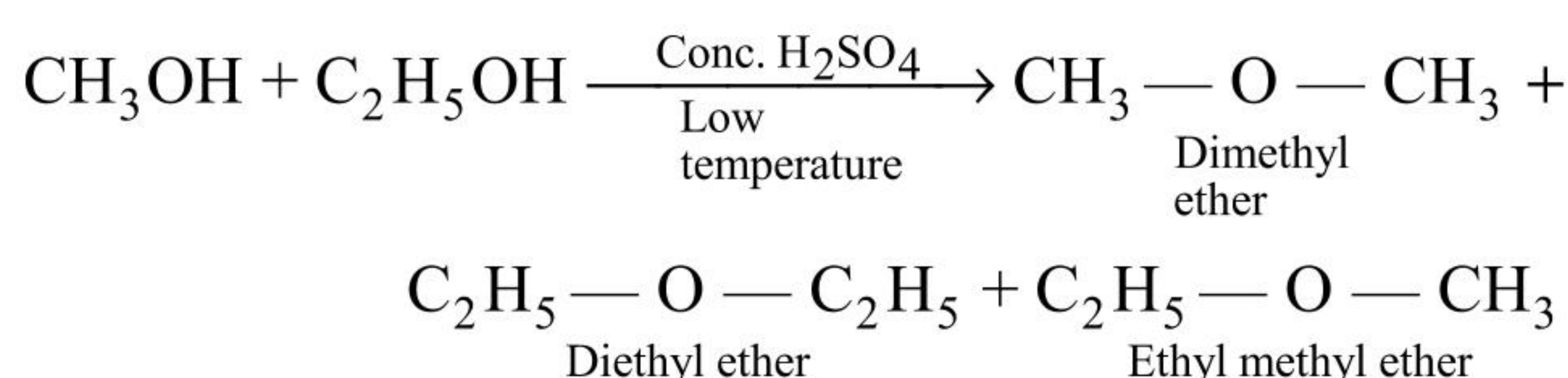
ii. Similarly, 3° alcohols give alkene instead of ethers.



4.26.2 LIMITATIONS

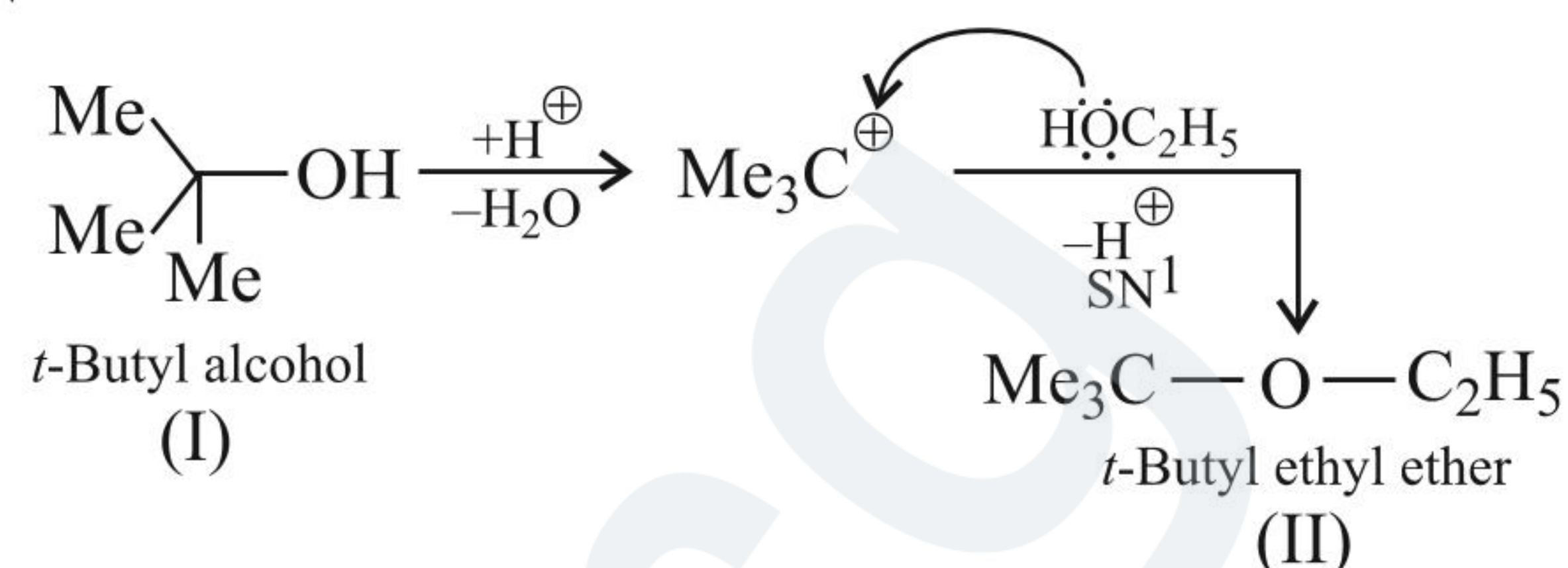
This method is not suitable for the preparation of unsymmetrical ethers by heating a mixture of ROH and R'OH with acid, because a mixture of three ethers

R—O—R, R—O—R', and R'—O—R' is obtained.

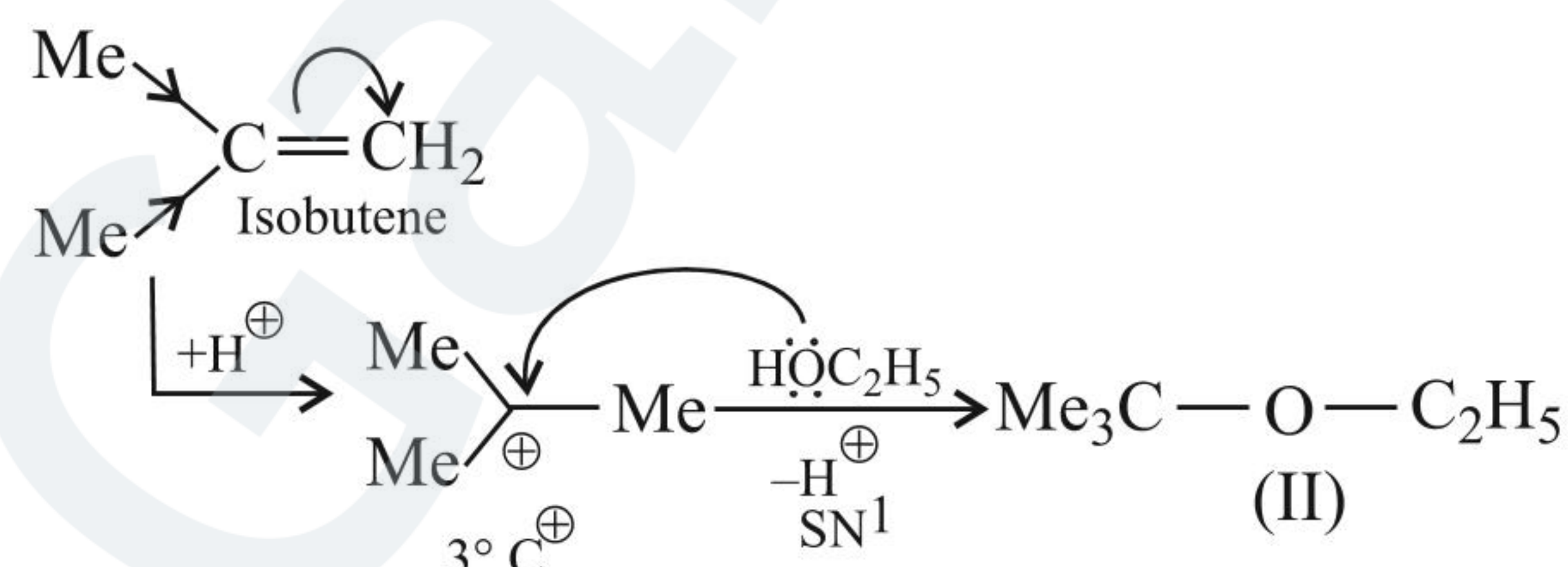


Preparation of *t*-butyl ethyl ether:

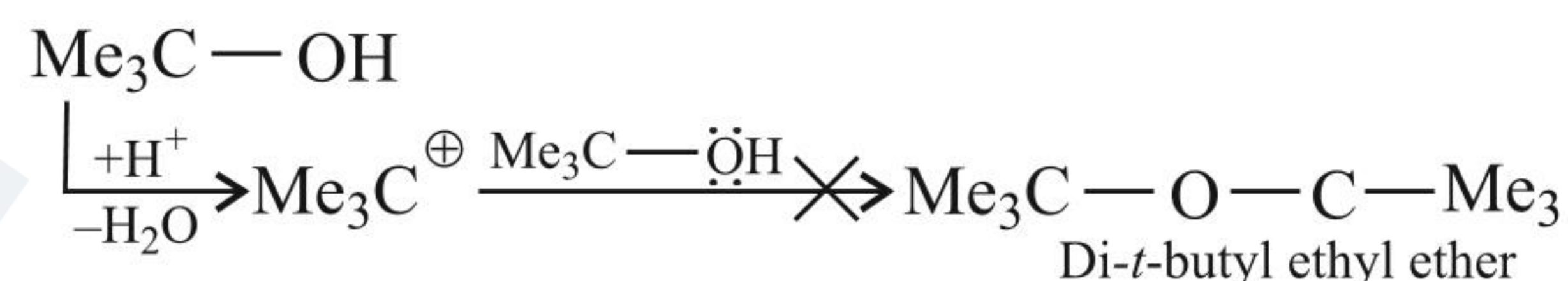
When one alcohol is 3°, its onium ion easily loses water to form C⁺, which is solvated by the other 2° and 1° alcohol to give unsymmetrical (or mixed) ether mainly. The reaction takes place by S_N1 mechanism.



However, (II) can be prepared by heating isobutene (Me₂C=CH₂) and C₂H₅OH with acid. The addition of H⁺ to the alkene gives Me₃C⁺ intermediate which is solvated by C₂H₅OH.

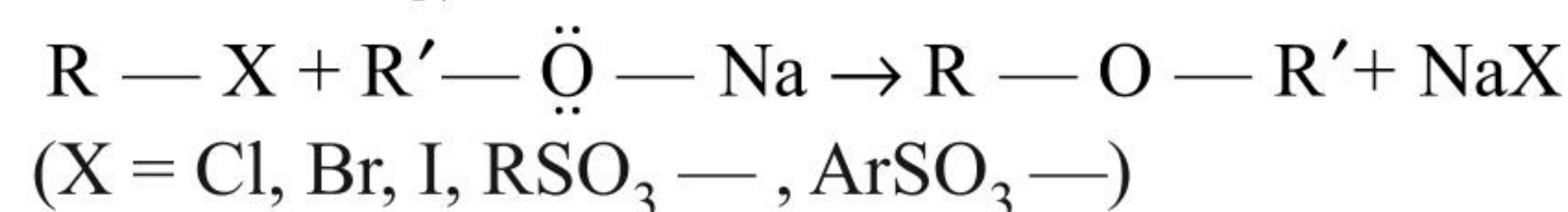


But di-*t*-butyl ether cannot be prepared by the above reaction because *t*-butanol cannot solvate 3° C⁺ readily because of steric hindrance.

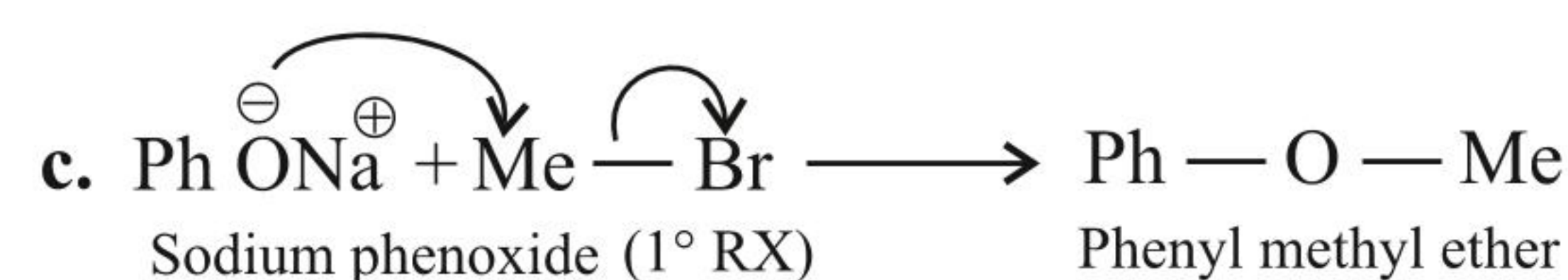
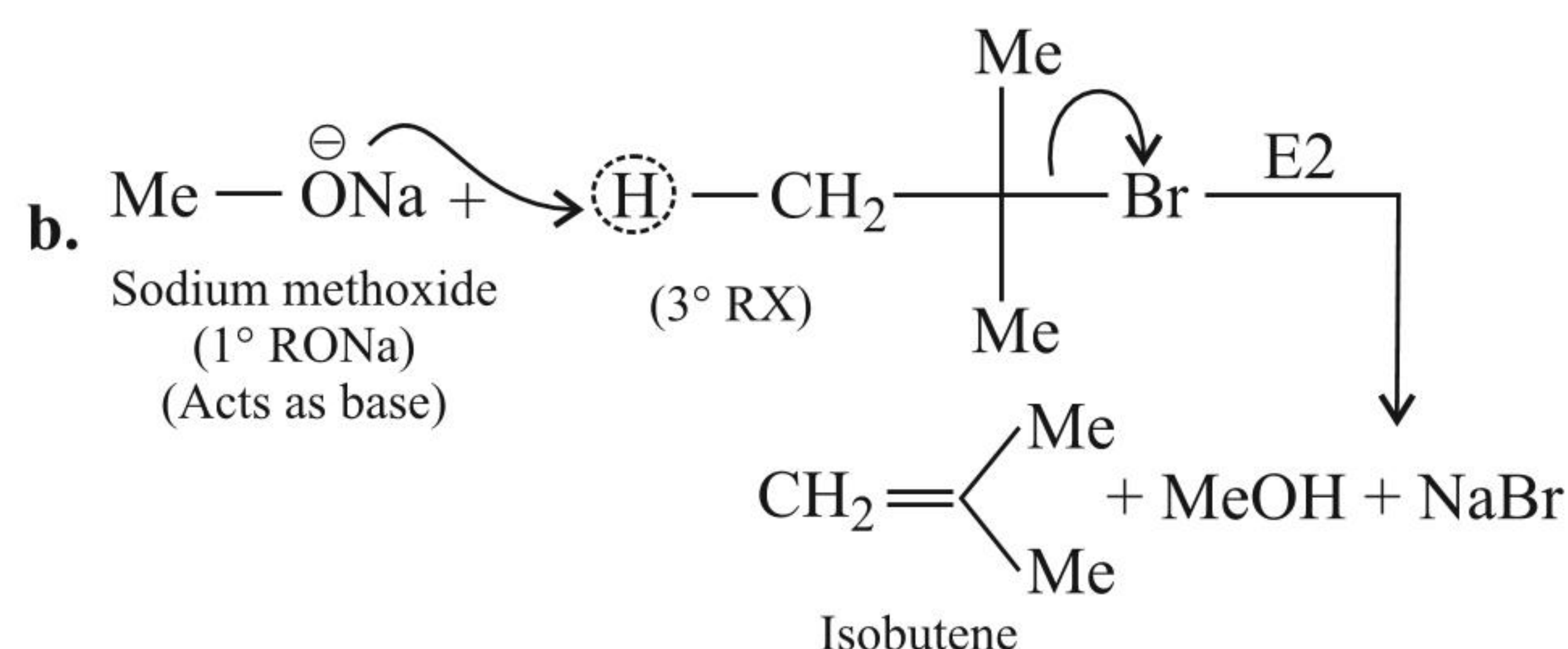
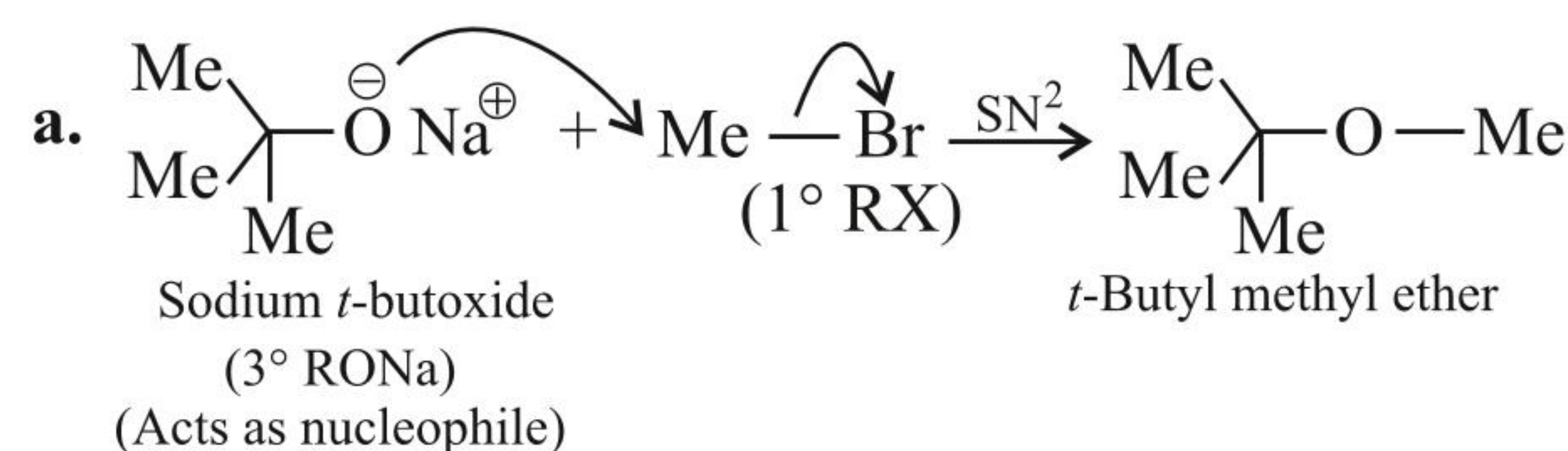


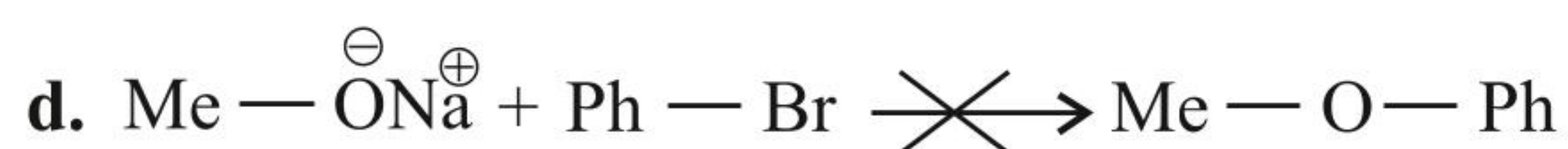
4.27 WILLIAMSON SYNTHESIS

It is a method for the preparation of symmetrical and unsymmetrical ethers in which RX is reacted with sodium alkoxide. The reaction proceeds via S_N2 mechanism.



1° RX and 3° R'ONa give better yield of ethers. In case of 2° RX or 3° RX, elimination competes over substitution reaction. If 3° RX is used, alkene is obtained and no ether is formed. For example,





Aryl halides do not undergo ArSN reaction unless the arylhalide is activated by the presence of EWG (e.g., $-\text{NO}_2$) at *o*- and *p*- position.

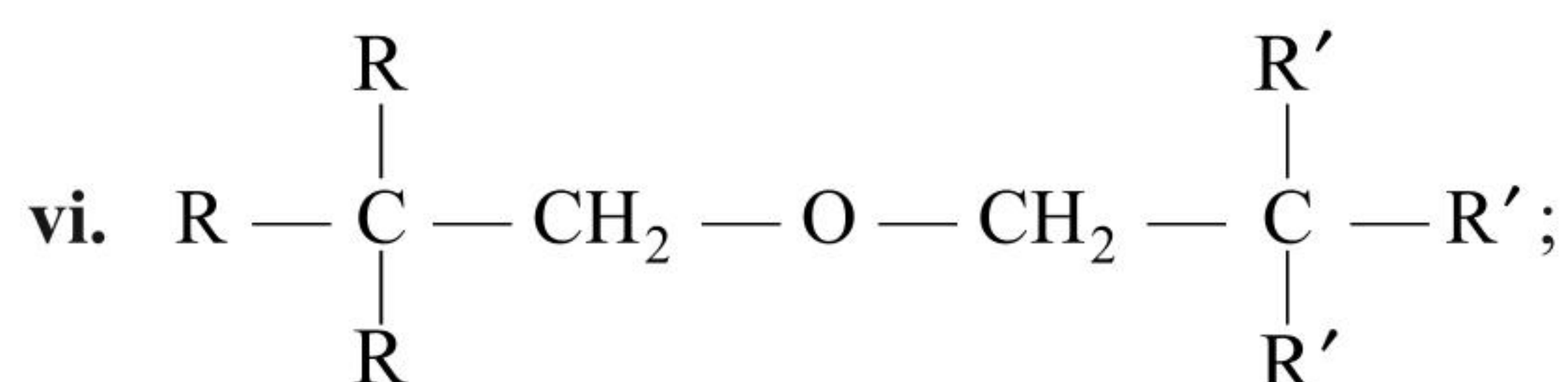
ILLUSTRATION 4.18

- Prepare the following ethers *via* Williamson's synthesis.
 - Di-*n*-propyl ether (A)
 - Benzyl methyl ether (B)
 - Phenylethyl ether (C)
 - t*-Butyl ethyl ether (D)
- Which compound in the above problem can be prepared by alternative Williamson's reaction?
- Explain the inability of (A), (C), and (D) in the above problem to be prepared *via* alternate Williamson's synthesis.
- Give six types of ethers that cannot be synthesised by the typical Williamson's synthesis.
- Rank the following alkyl halides in the decreasing order of reactivity in Williamson's reaction.
 $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$ (A); $\text{ClCH}_2\text{CH}=\text{CH}_2$ (B);
 $\text{ClCH}_2\text{CH}_2\text{CH}_3$ (C); $\text{BrCH}_2\text{CH}_2\text{CH}_3$ (D)

Sol.

- $n\text{-PrOH} \xrightarrow{\text{Na}} n\text{-PrO}^- \xrightarrow{n\text{-PrBr}} \text{PrOPr}$ (A)
 - $\text{MeOH} \xrightarrow{\text{Na}} \text{MeO}^- \xrightarrow{\text{PhCH}_2\text{Br}} \text{PhCH}_2\text{OMe}$ (B)
 - $\text{PhOH} \xrightarrow{\text{NaOH}} \text{PhO}^- \xrightarrow{\text{EtBr}} \text{PhOEt}$ (C)
 - $t\text{-BuOH} \xrightarrow{\text{Na}} t\text{-BuO}^- \xrightarrow{\text{EtBr}} t\text{-BuOEt}$ (D)

This reaction gives a poor yield because of the bulkiness of $t\text{-BuO}^-$.
- Only (B): $\text{PhCH}_2\text{OH} \xrightarrow{\text{Na}} \text{PhCH}_2\text{O}^- \xrightarrow{\text{MeBr}} \text{Ph-CH}_2\text{OMe}$ (B)
- (A) is a simple ether.
 - Aryl halides do not undergo nucleophilic displacement (S_N) reaction.
 - EtO^- is a strong base as well as a nucleophile and dehydrohalogenates *t*-butylchloride in completing E_2 reaction, giving alkene and little or no ether.
- $\text{R}_2\text{CH}-\text{O}-\text{CHR}_2$; both C atoms are 2° .
 - $\text{R}_2\text{CH}-\text{O}-\text{CR}_3$; one C is 2° and one is 3° .
 - $\text{R}_3\text{C}-\text{O}-\text{CR}_3$; both C atoms are 3° .
 - $\text{Ar}-\text{O}-\text{Ar}$; both diaryl ethers groups, **but ethers are formed if ArX contains EWG at *o* & *p*-position.**
 - $\text{R}-\text{CH}=\text{CH}-\text{O}-\text{CH}=\text{CH}-\text{R}'$; vinyl halides do not undergo S_N reaction.



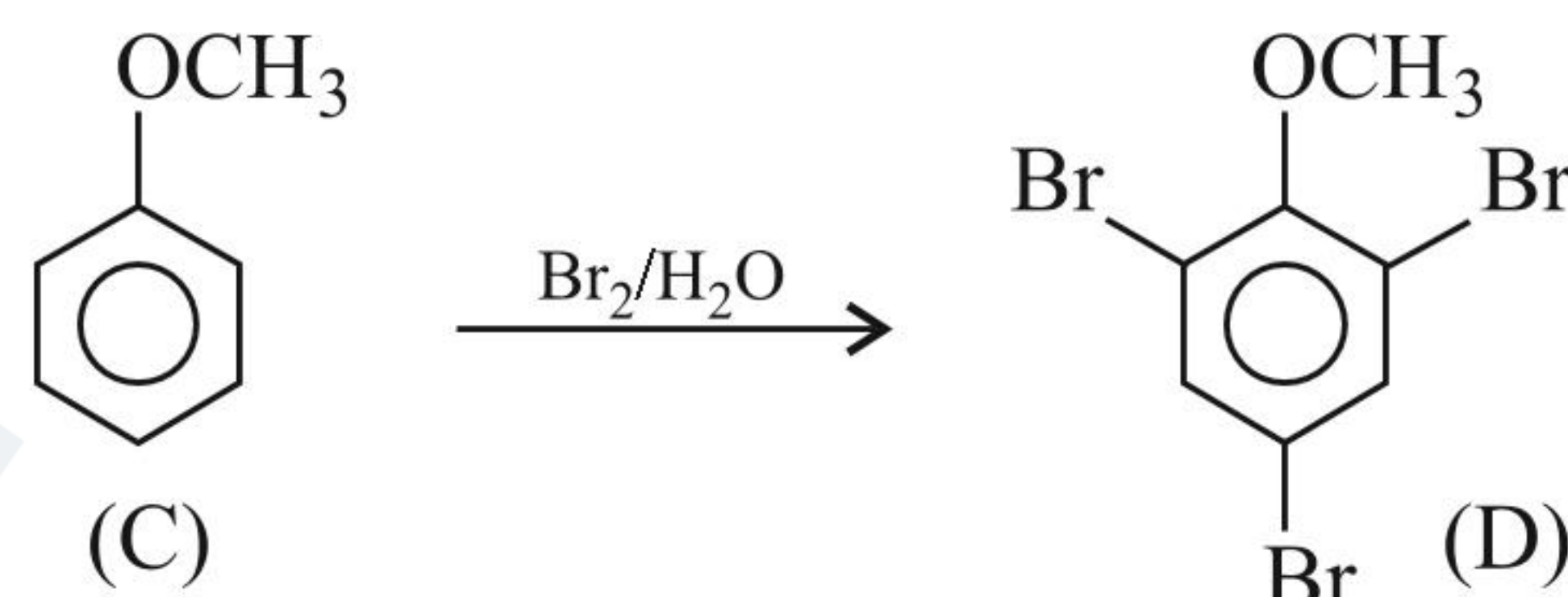
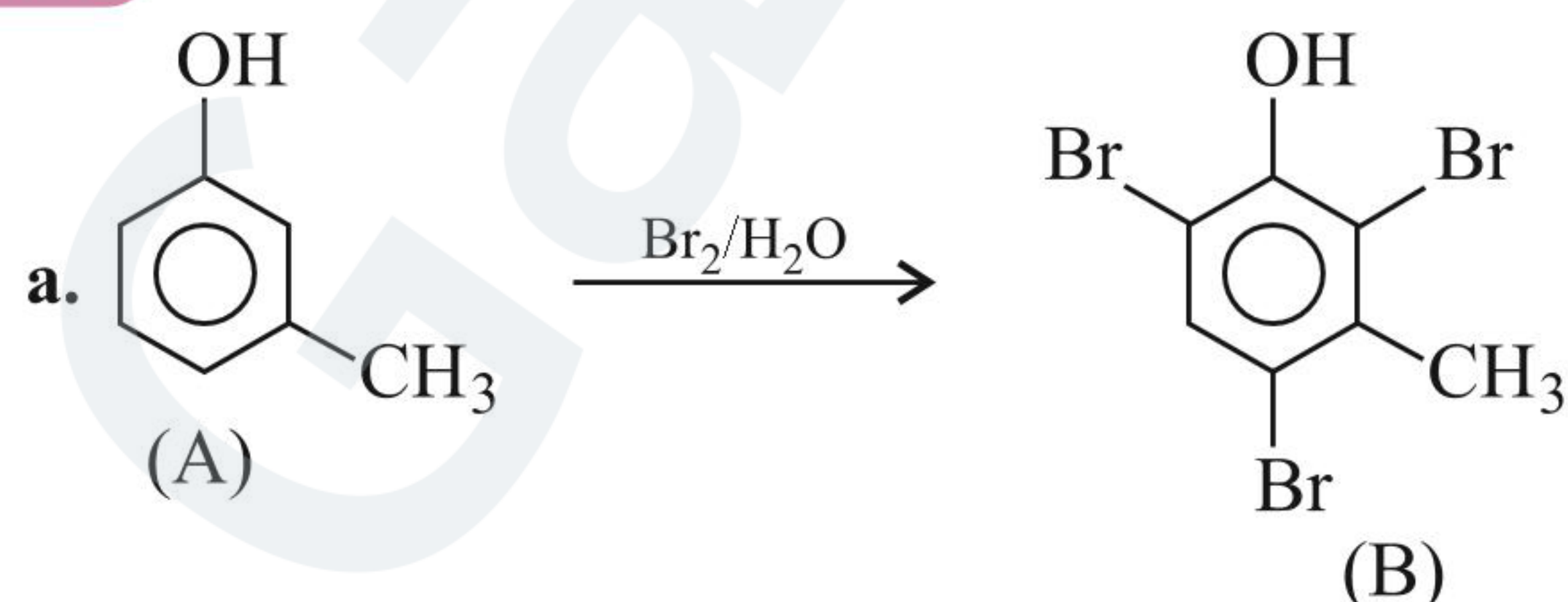
Neopentyl type halides are inert to $\text{S}_\text{N}2$ reaction.

- e. (B) > (D) > (C) > (A). Allylic > bromide > chloride > neopentyl (too hindered).

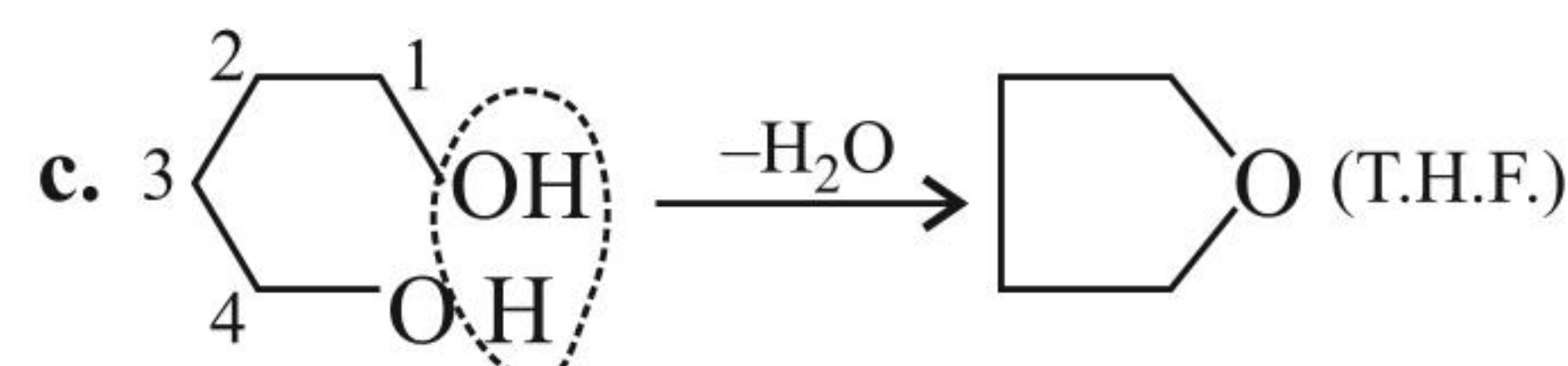
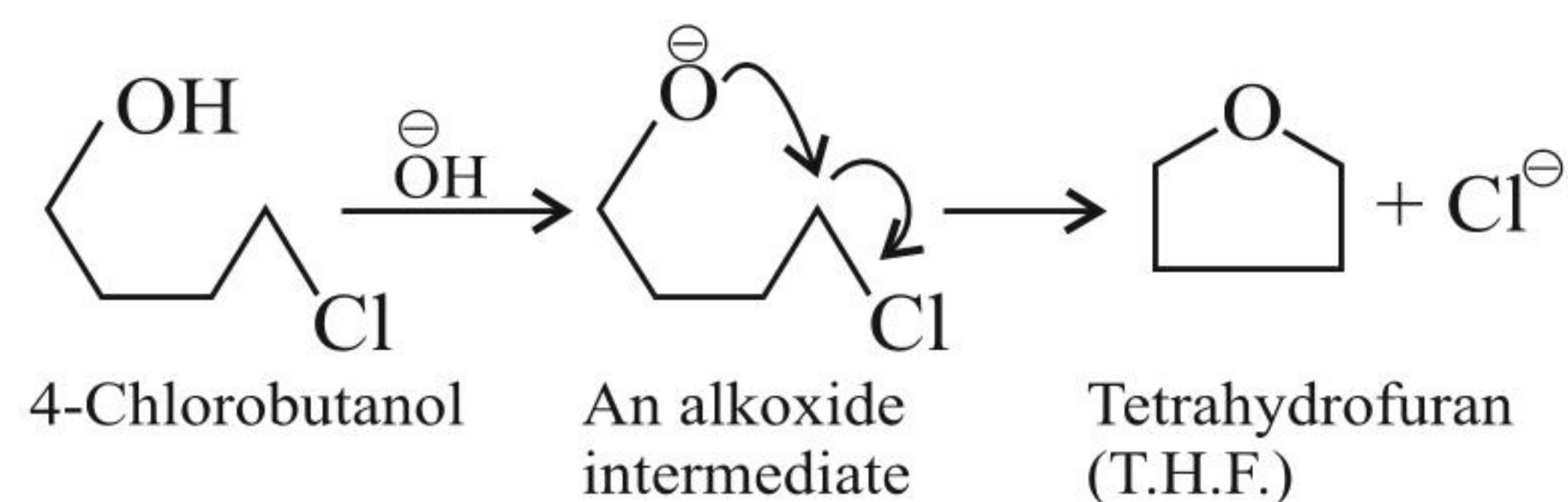
ILLUSTRATION 4.19

- An aromatic compound (A) ($\text{C}_7\text{H}_8\text{O}$) on reaction with $\text{Br}_2 + \text{H}_2\text{O}$ gives a white ppt. of compound (B) ($\text{C}_7\text{H}_5\text{OBr}_3$). Compound (A) is soluble in NaOH. Compound (C), an isomer of (A), also gives the same reaction and gives a white ppt. of compound (D) ($\text{C}_7\text{H}_5\text{OBr}_3$). Compound (C) is insoluble in NaOH. Identify (A), (B), (C), and (D).
- $4\text{-Chlorobutanol} \xrightarrow{\text{OH}^-} (\text{A}) \longrightarrow (\text{B}) + \text{Cl}^-$
- $\text{HOCH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH} \xrightarrow[160-170^\circ\text{C}]{\text{Conc. H}_2\text{SO}_4}$

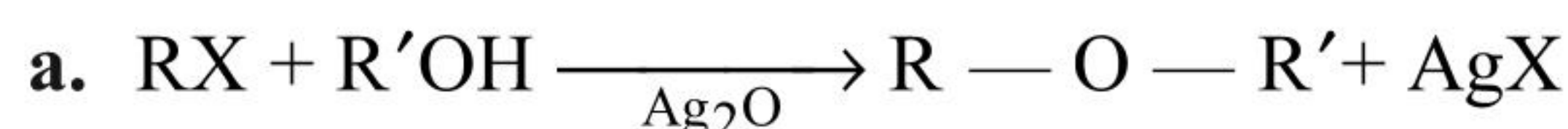
Sol.



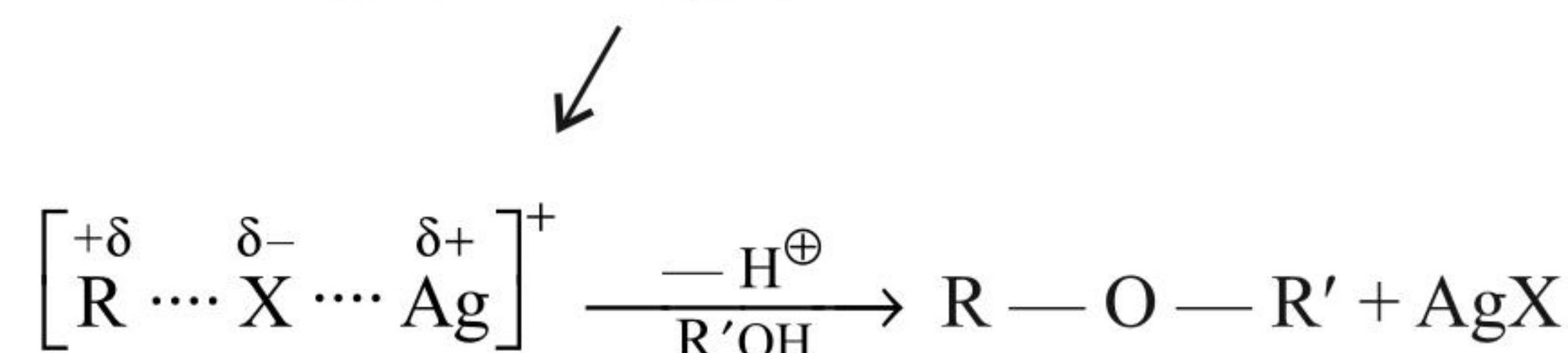
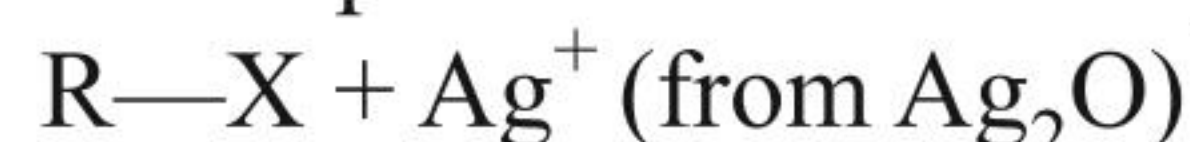
- b. This is an example of intramolecular Williamson's reaction.

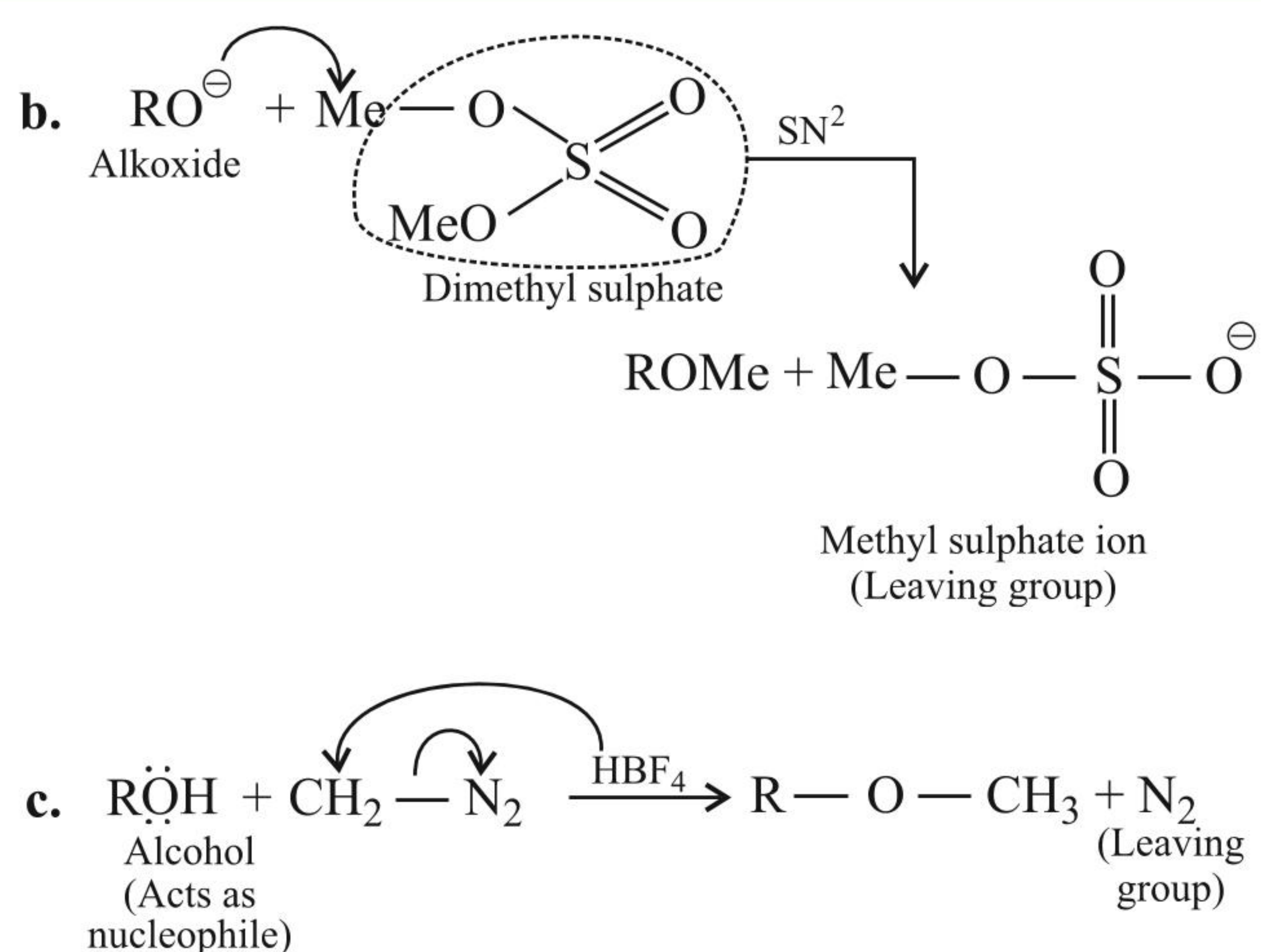


4.28 SOME OTHER METHODS FOR THE PREPARATION OF ETHERS

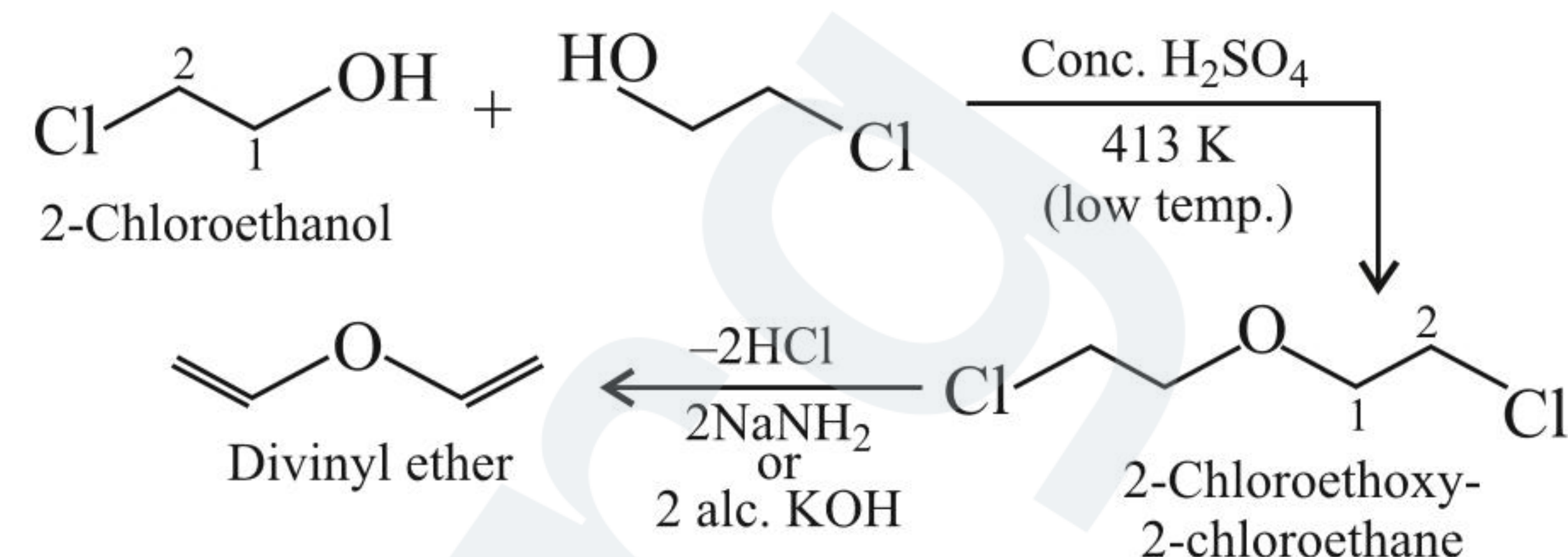


Ag_2O catalyses the removal of halide ion as AgX . The ($-\text{OH}$) group of ROH then acts as a strong enough nucleophile to affect the $\text{S}_\text{N}2$ reaction.



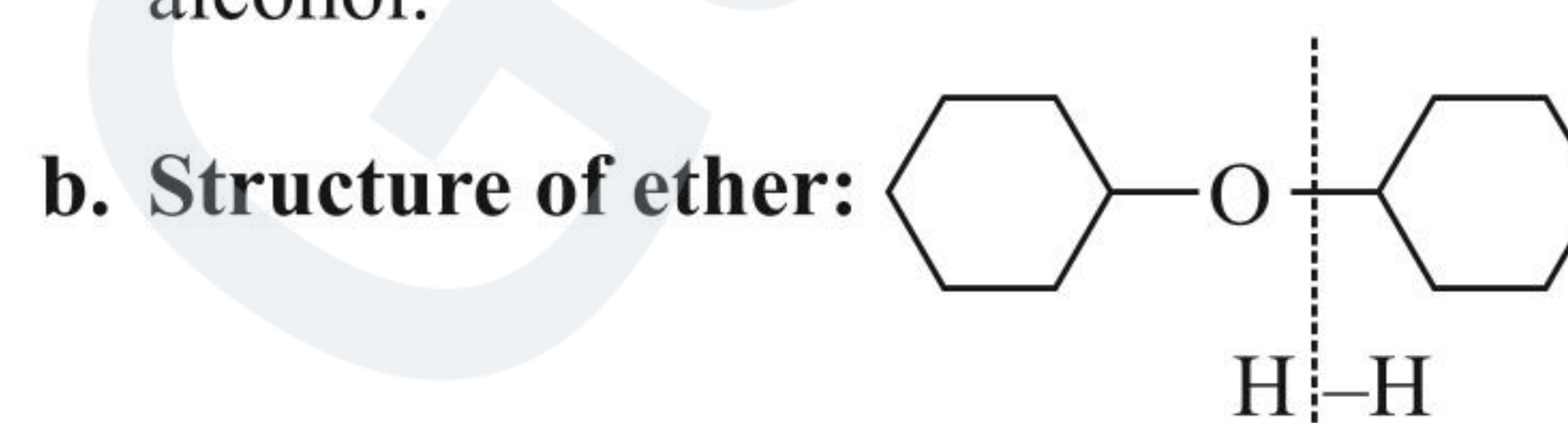


Vinyl alcohol $\left(\text{CH}_2=\text{CH}-\text{OH} \right)$ cannot be used as reactant since it is an unstable compound and tautomerise to $\text{H}_3\text{C}-\text{CH}=\text{O}$. Double bond is introduced after the formation of ether by method (III).

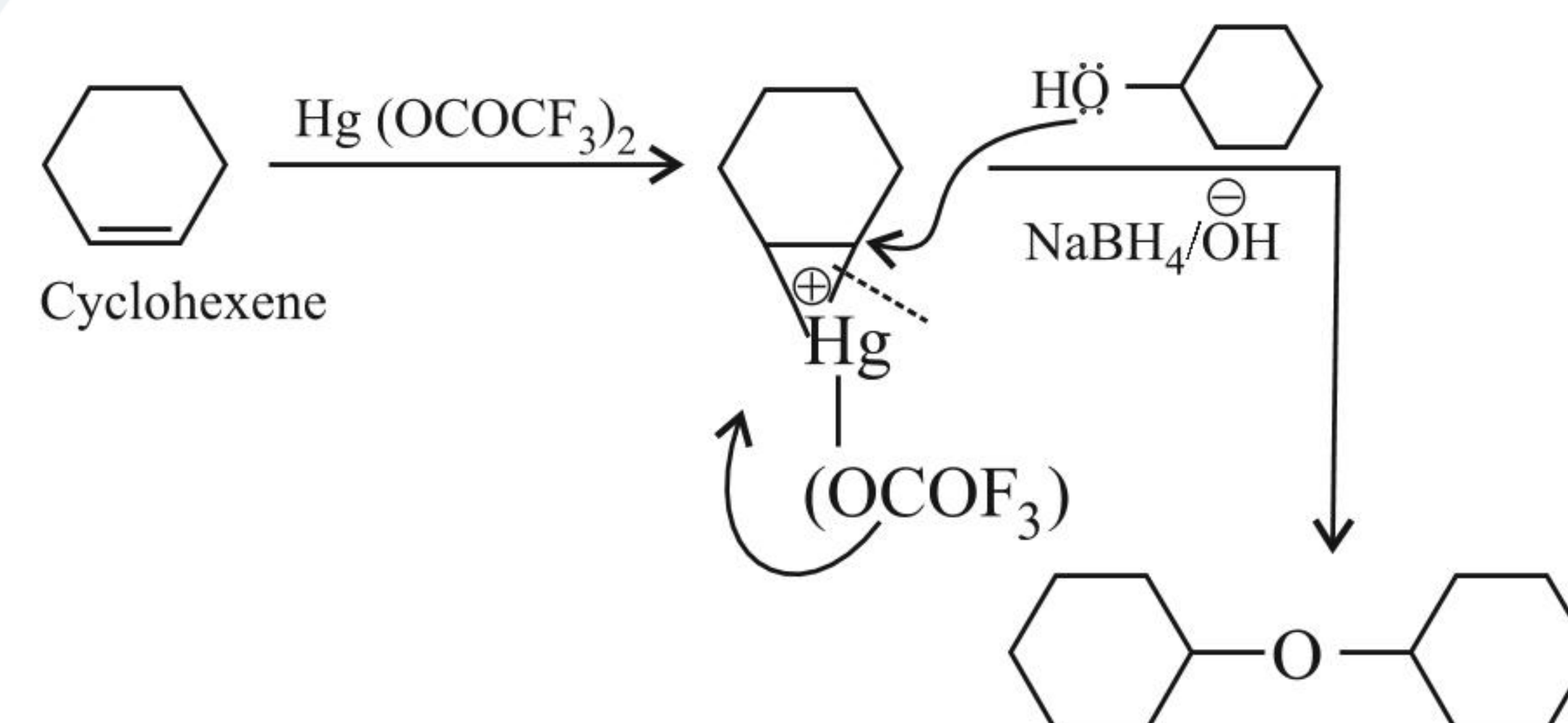
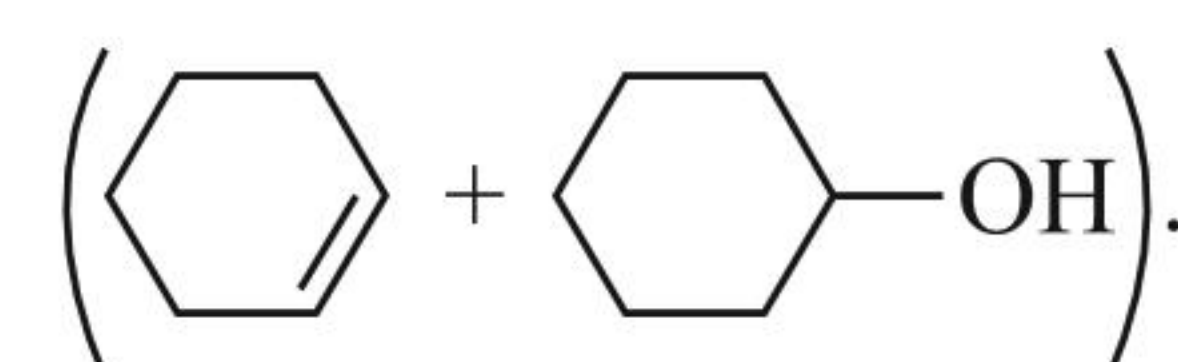


Method (I) cannot be used because of unreactive vinyl halide $\left(\text{CH}_2=\text{CH}-\text{Cl} \right)$ and vinyl oxide $\left(\text{CH}_2=\text{CH}-\text{O}^- \right)$; both are stabilised by resonance.

Method (II) cannot be used because of unreactive vinyl alcohol.



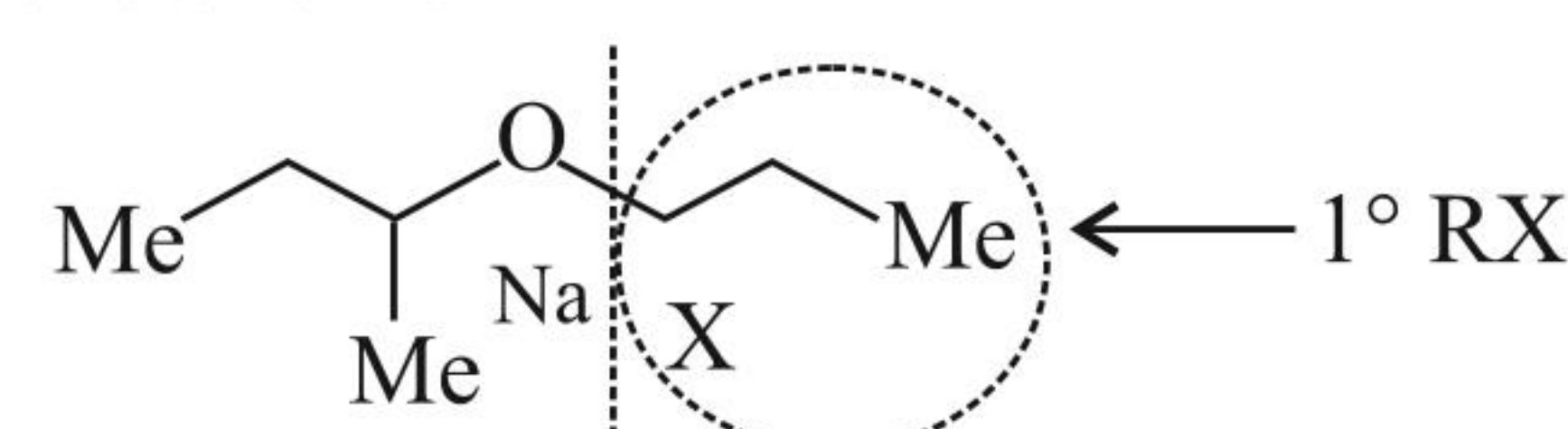
Method (II) will give desired result with



Although it is symmetrical ether, but method (III) cannot be used because intramolecular dehydration of 2° ROH would give mainly cyclohexene.

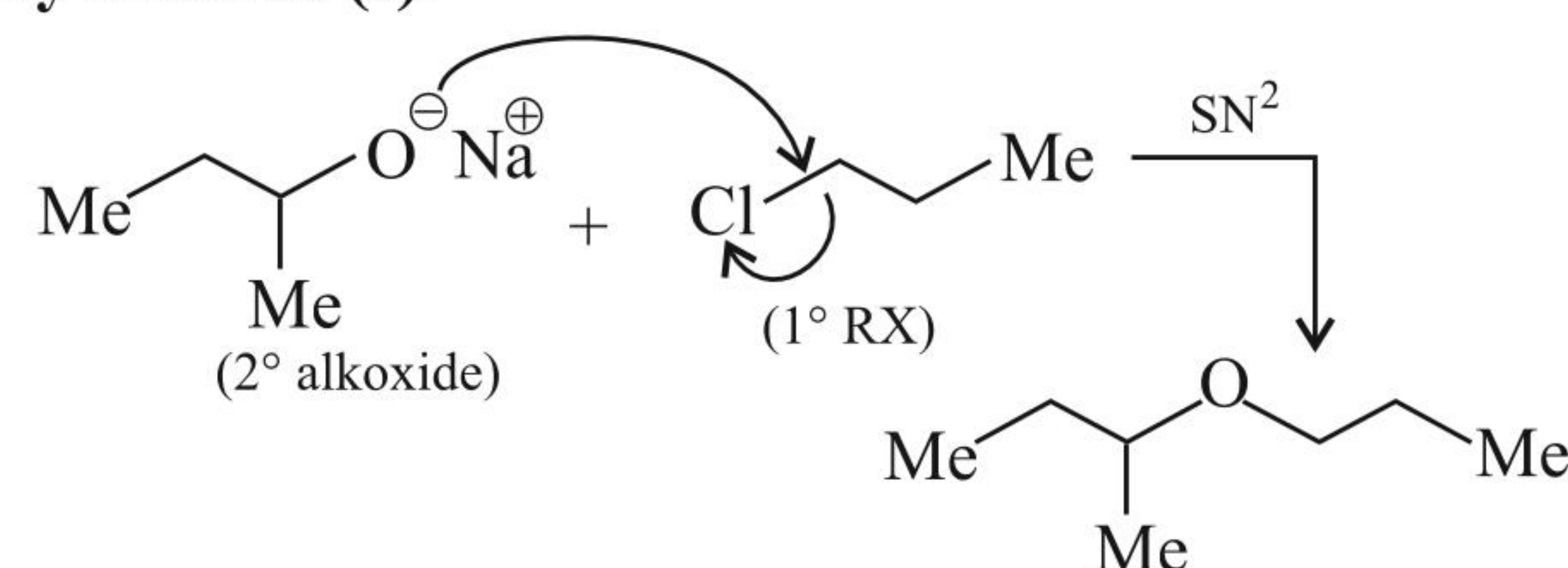
Method (I) cannot be used because 2° RX $\left(\text{C}_6\text{H}_{11}\text{Cl} \right)$ does not favour the reaction.

c. **Structure of ether:**

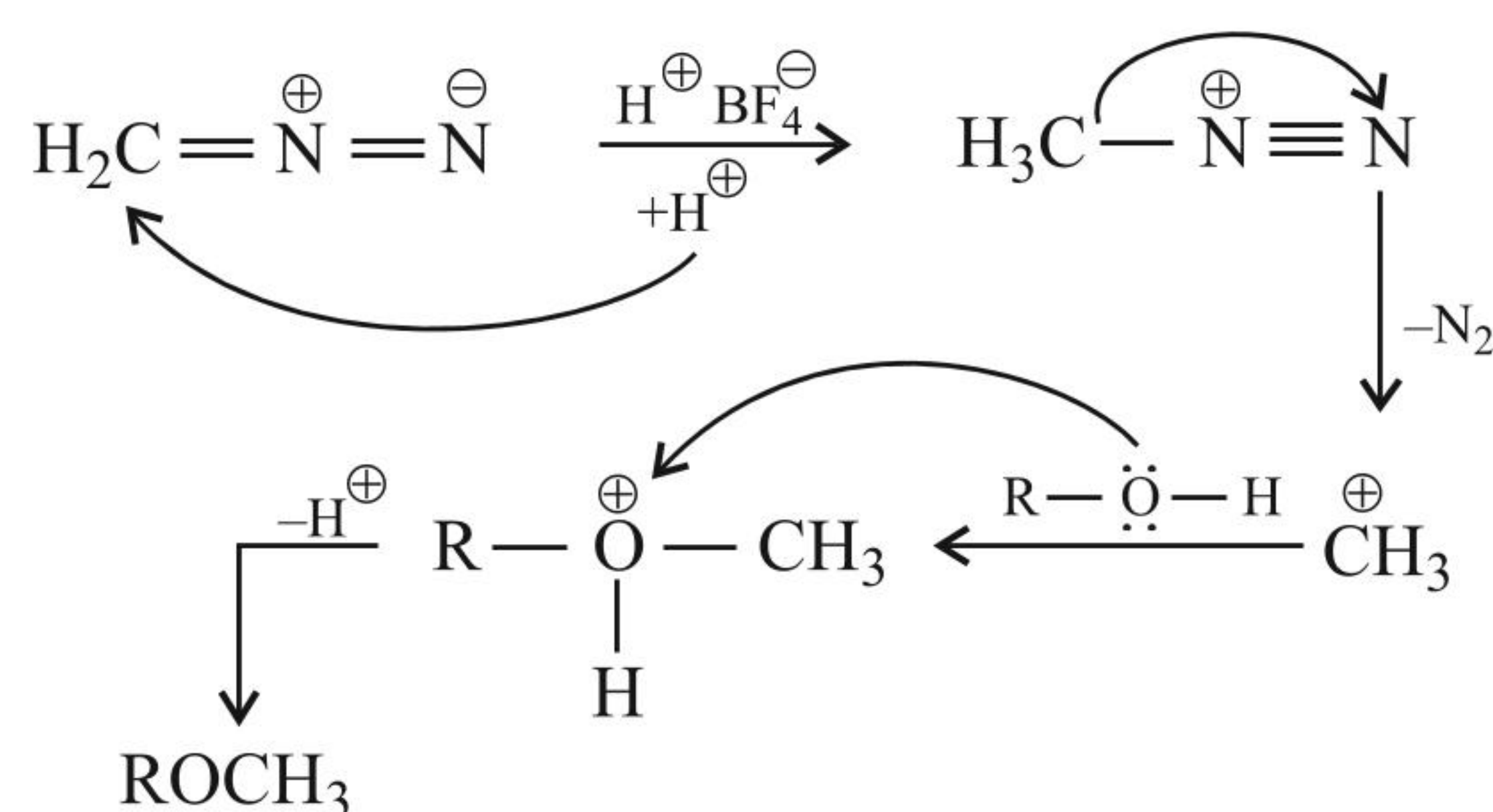


Both Methods (I) and II can be used.

By Method (I):

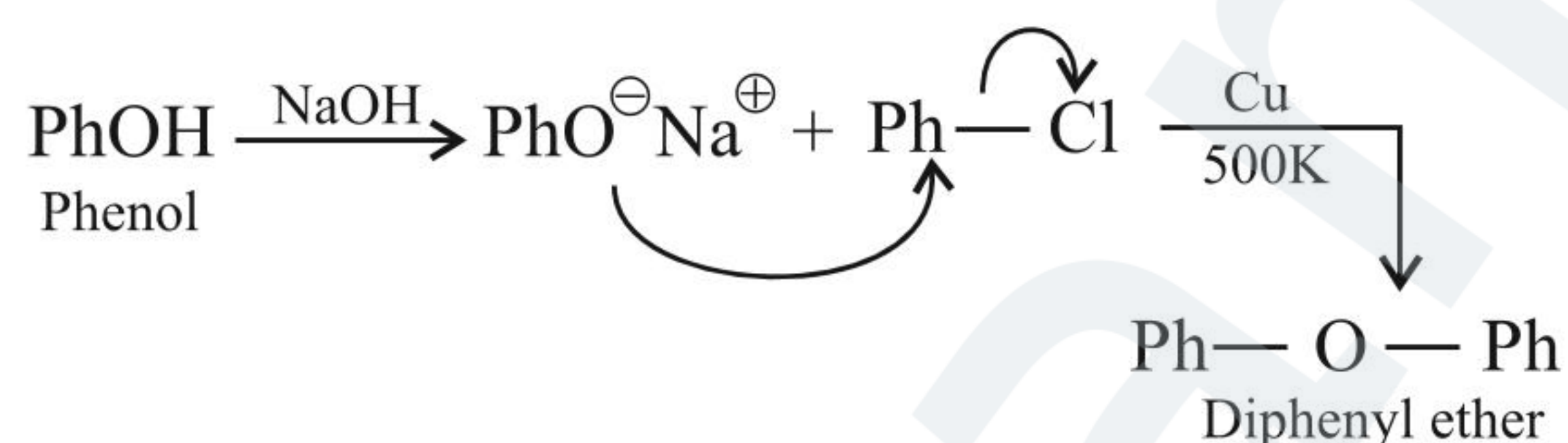


4.28.1 MECHANISM



4.28.2 COMMERCIAL SYNTHESIS OF DIPHENYL ETHER

Diphenyl ether is synthesised by a modification of the Williamson ether synthesis. In this process, the reaction takes place between phenol and chlorobenzene in the presence of base and catalytic copper. It proceeds by a benzyne type reaction (see Chapter 3).



For synthesis of ethers from Grignard reagent, see Section 1.7.5.

ILLUSTRATION 4.20

Synthesise the following ethers, selecting the given methods.

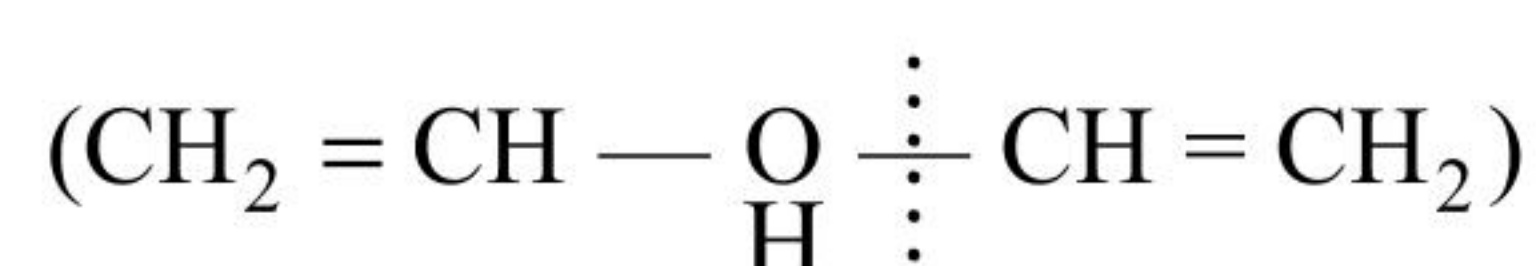
- Williamson's synthesis
- Alkoxy mercuriation-demercuration
- Intermolecular dehydration

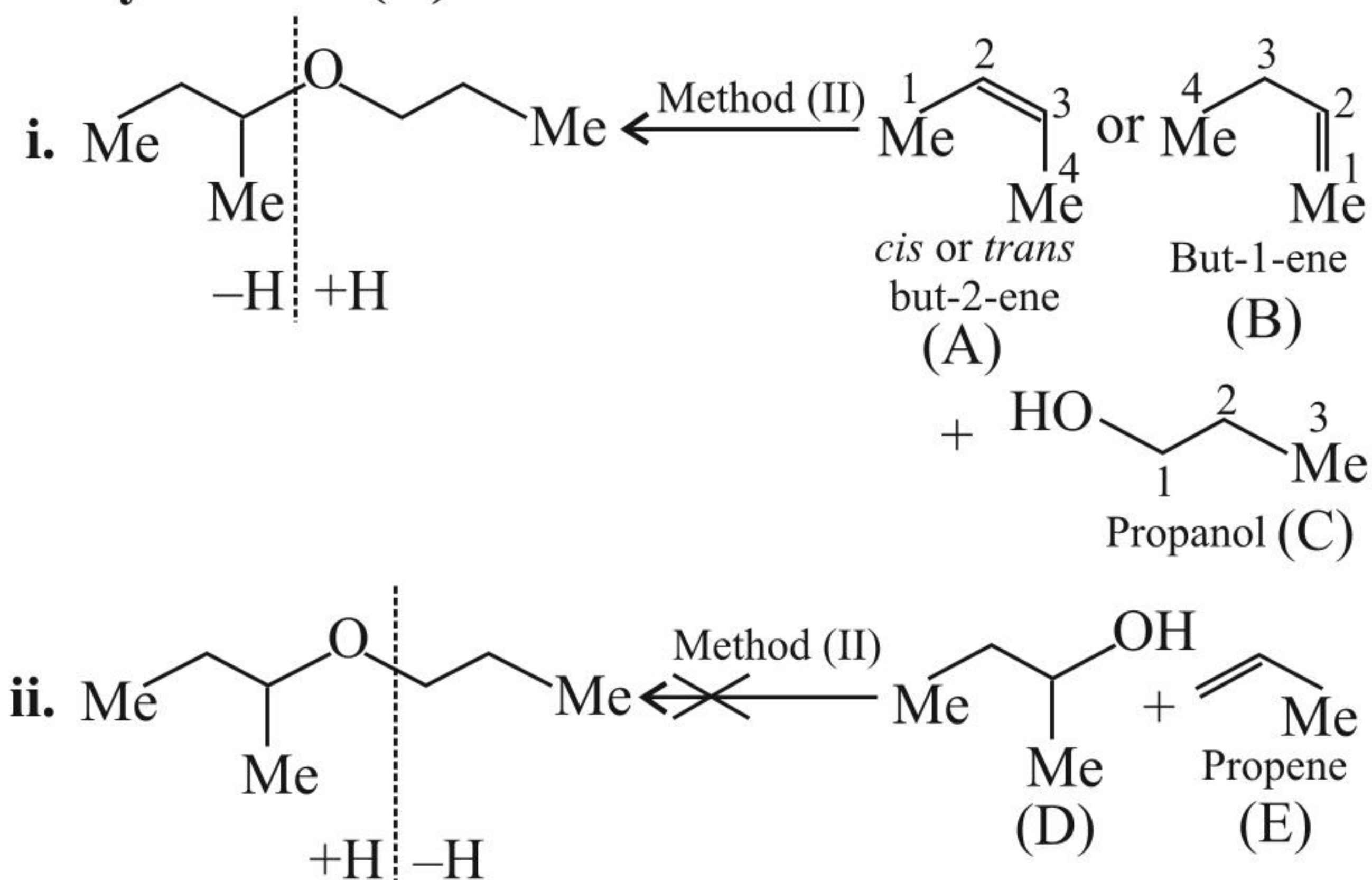
Give reasons for the selection of the method.

- Divinyl ether
- Dicyclohexyl ether
- Propyl *sec*-butyl ether
- 1-Propoxy-2-methyl propane

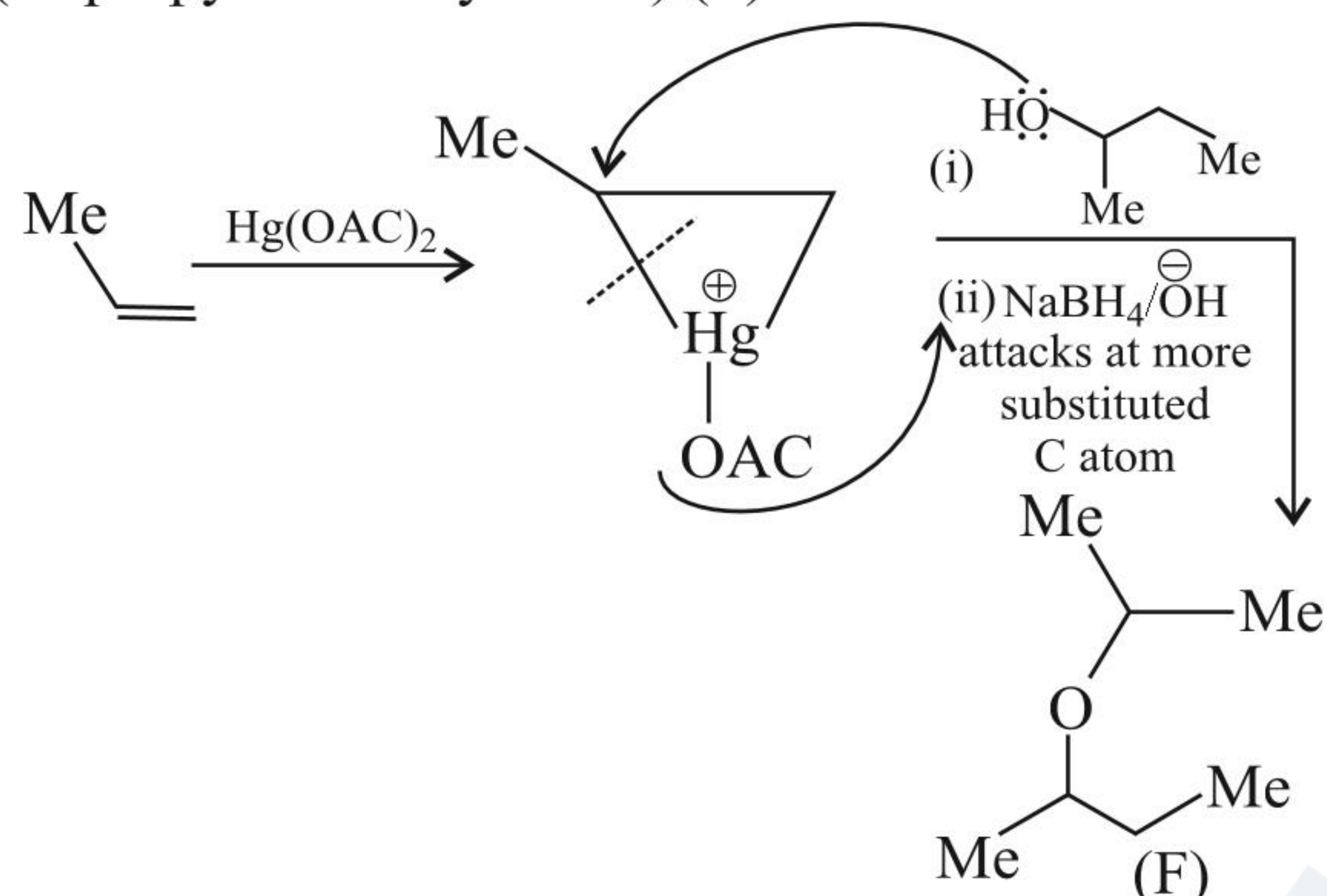
Sol.

a. **Write the structures of ether:**

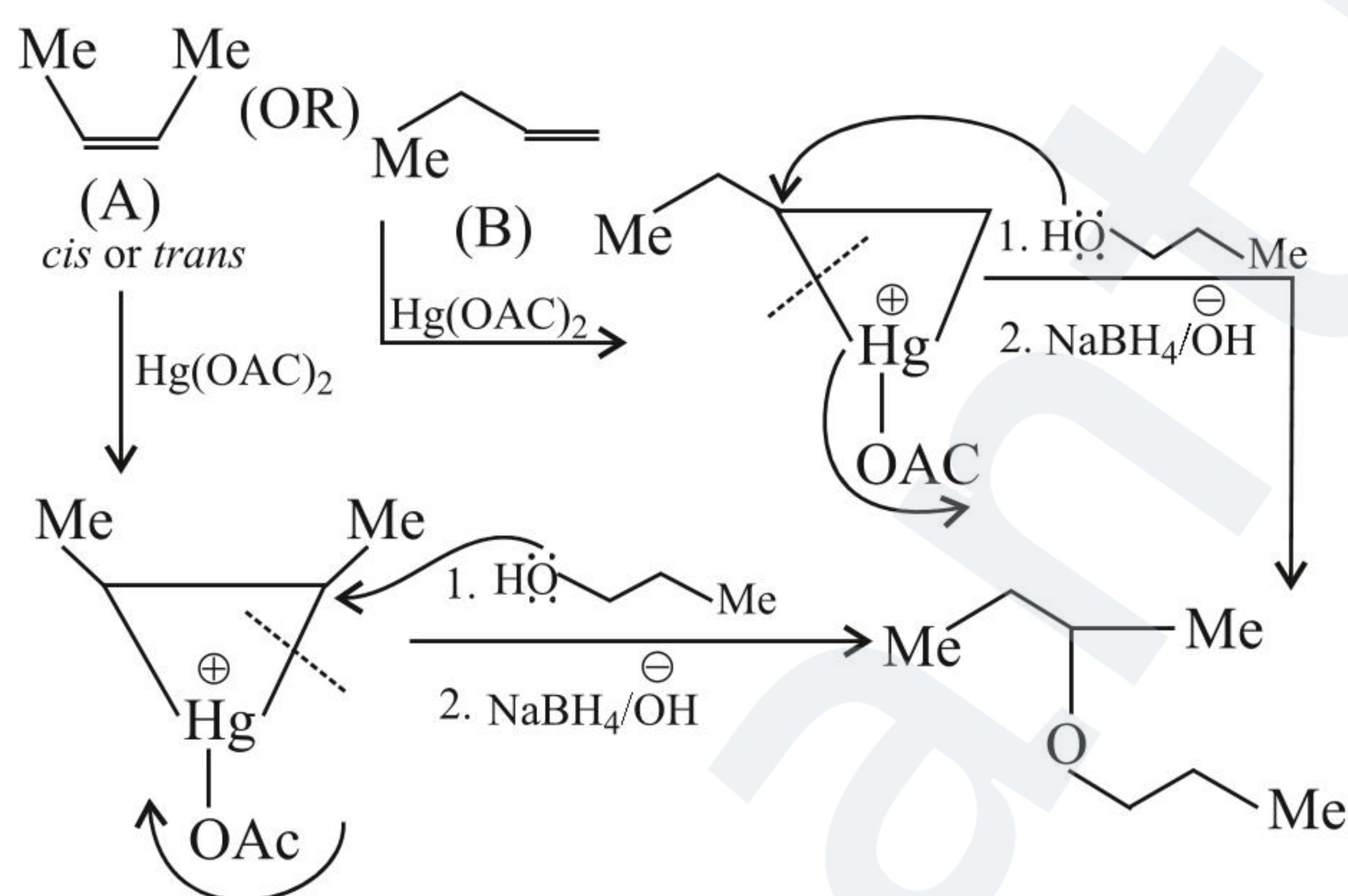
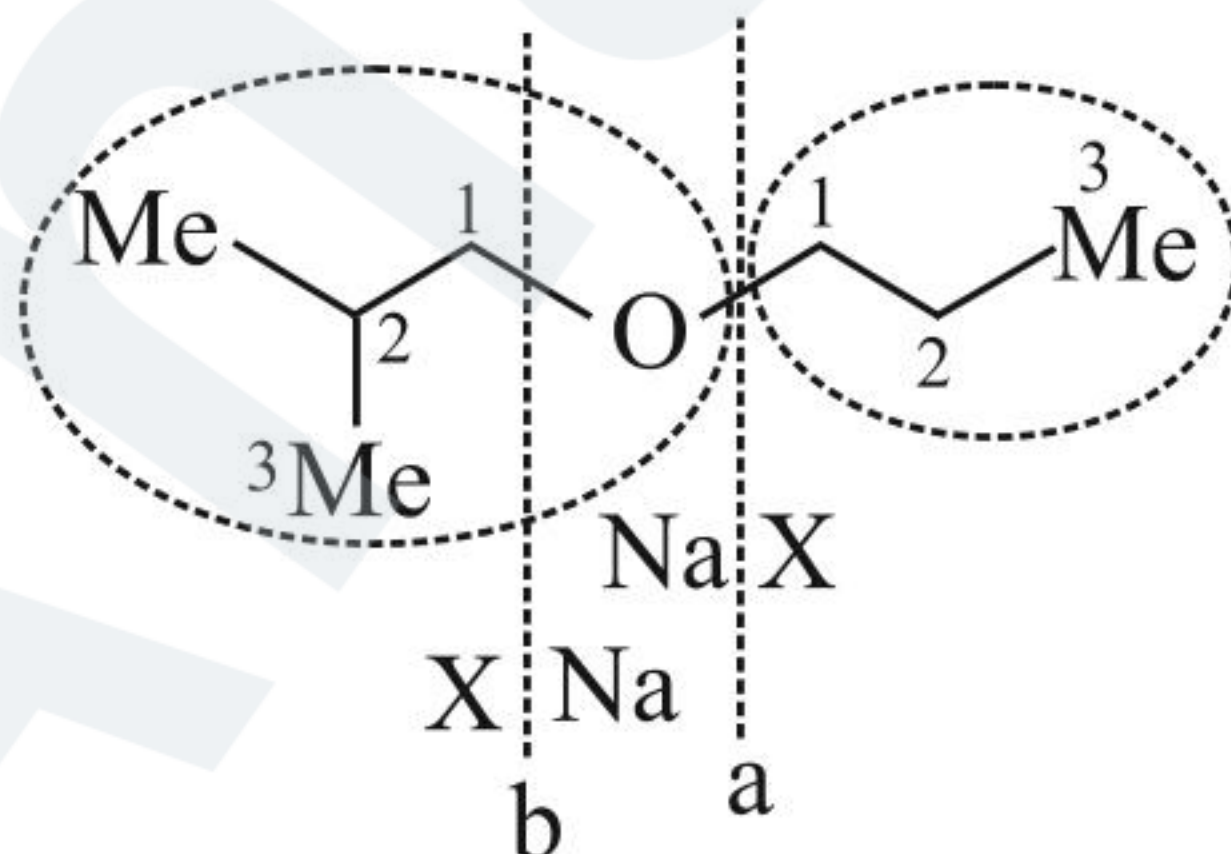


By method (II):

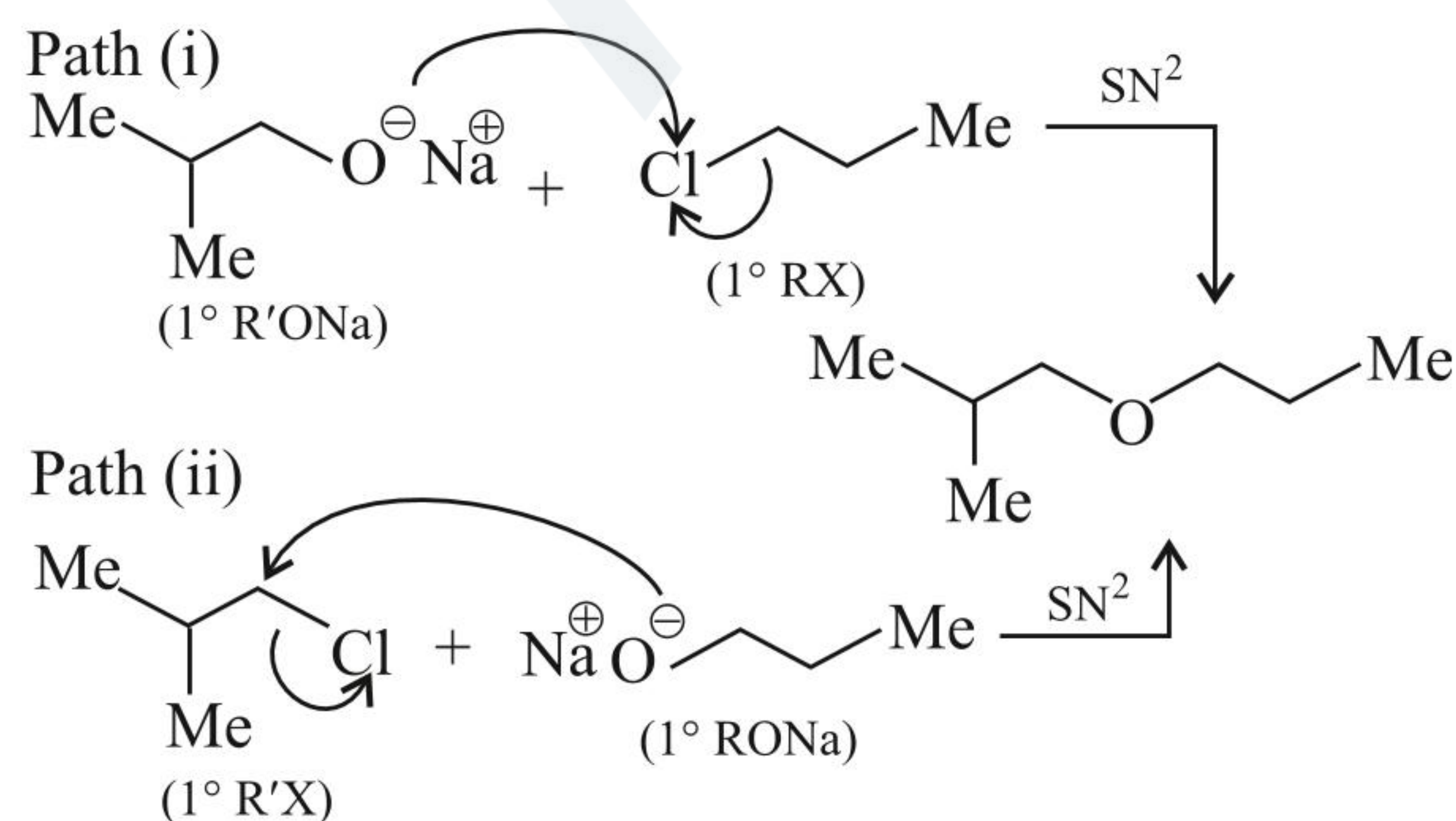
Path (ii) is not feasible because it would give different ether (isopropyl-*sec*-butyl ether) (F).



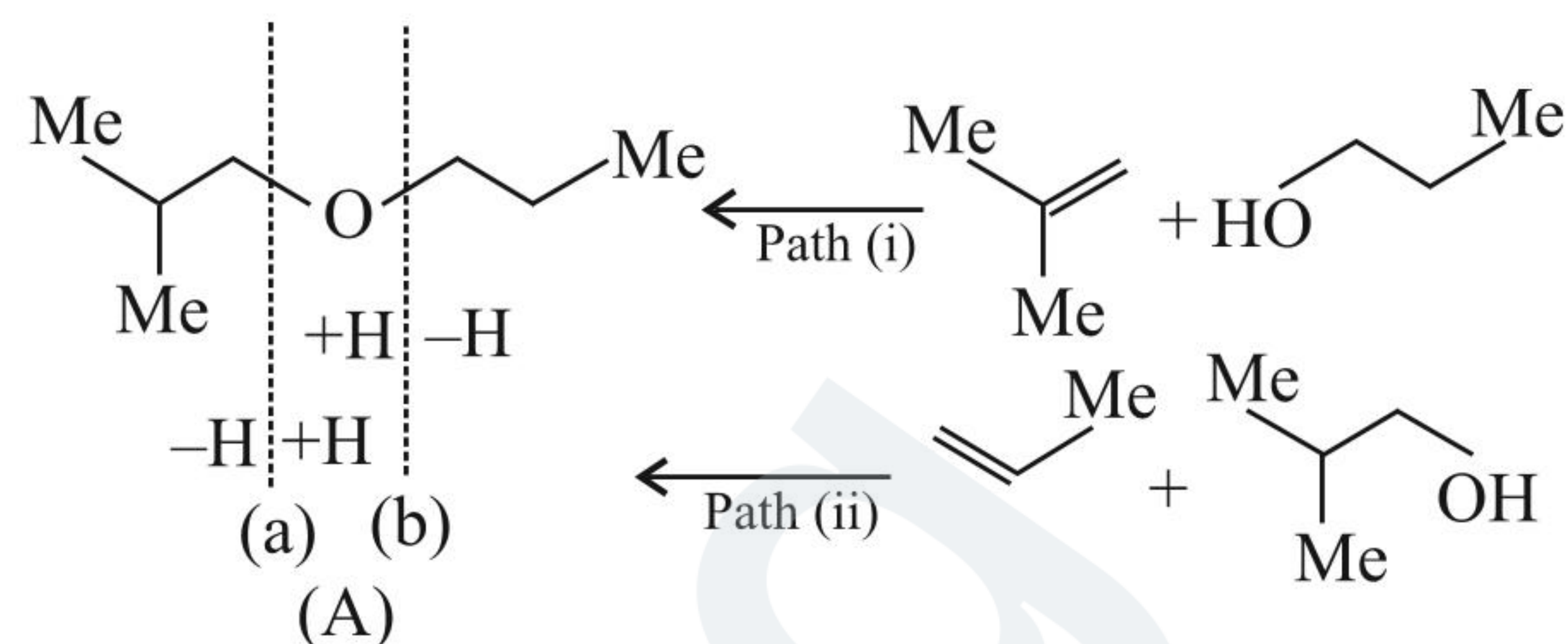
Path (i) would give the required ether:

**d. Structure of the ether:**

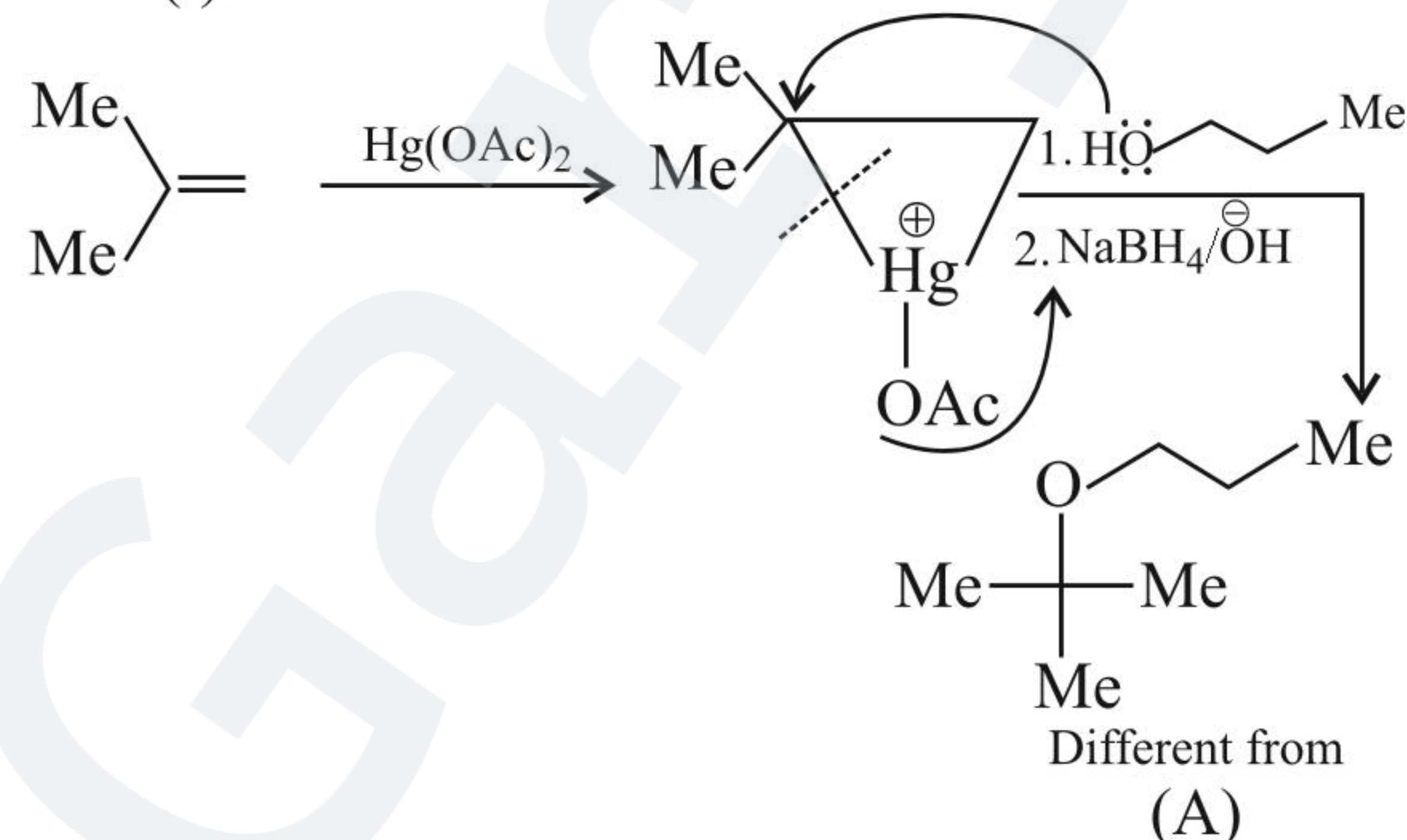
Method I is feasible:



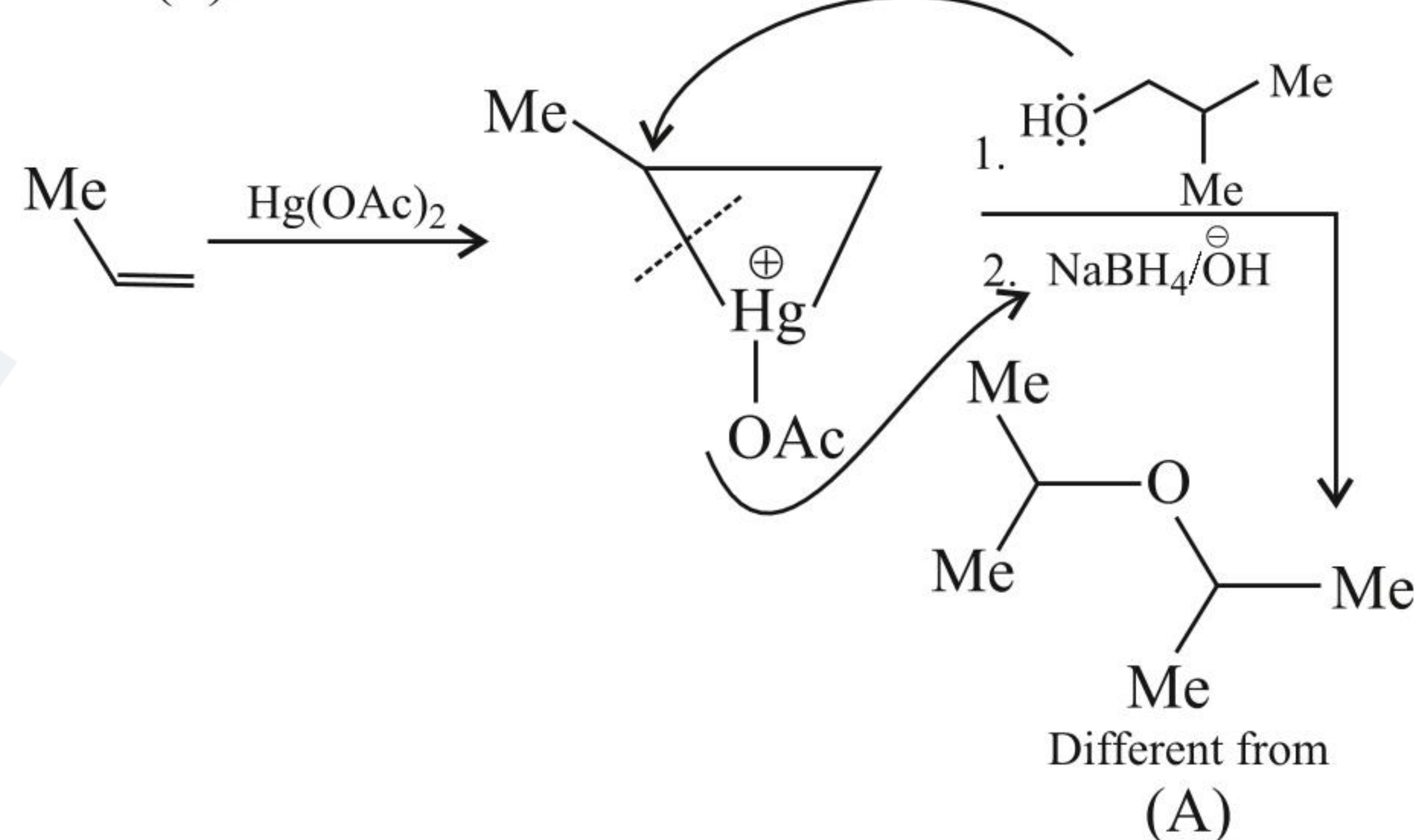
Methods II and III are not feasible and method II would give different isomers.



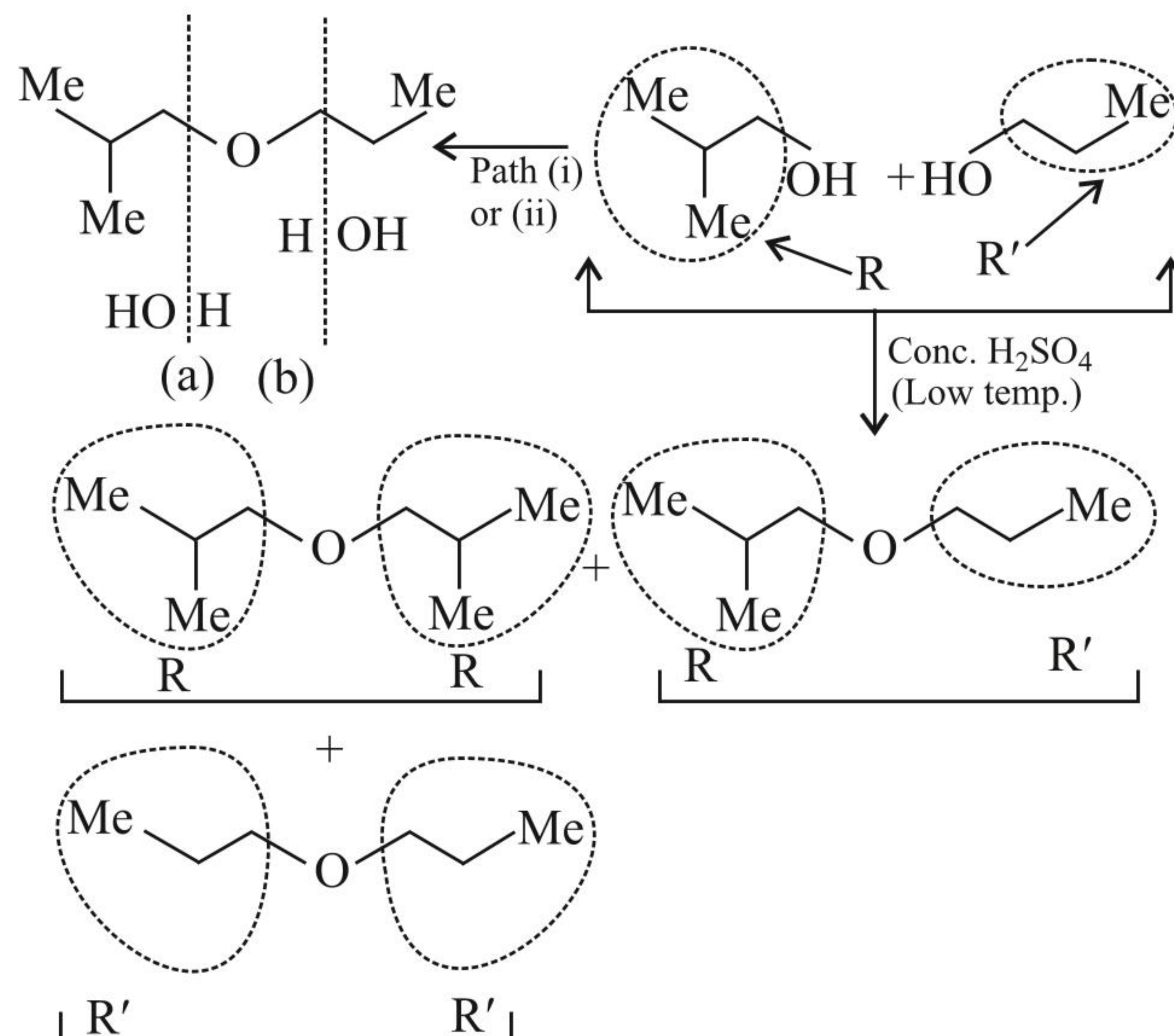
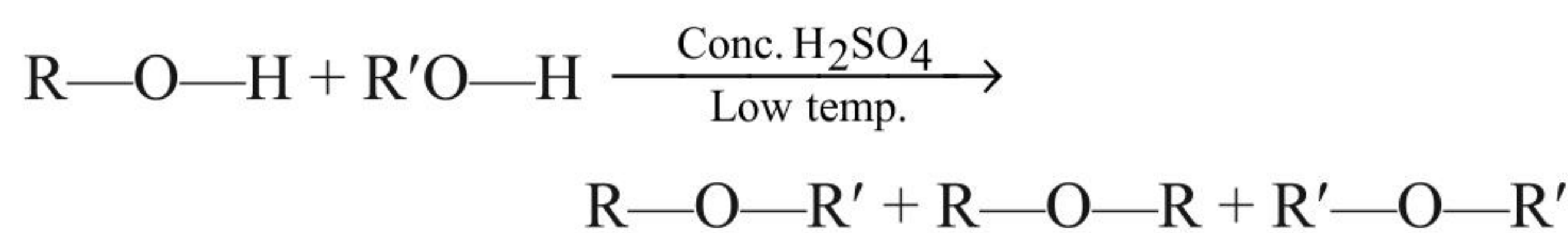
Path (i):



Path (ii):

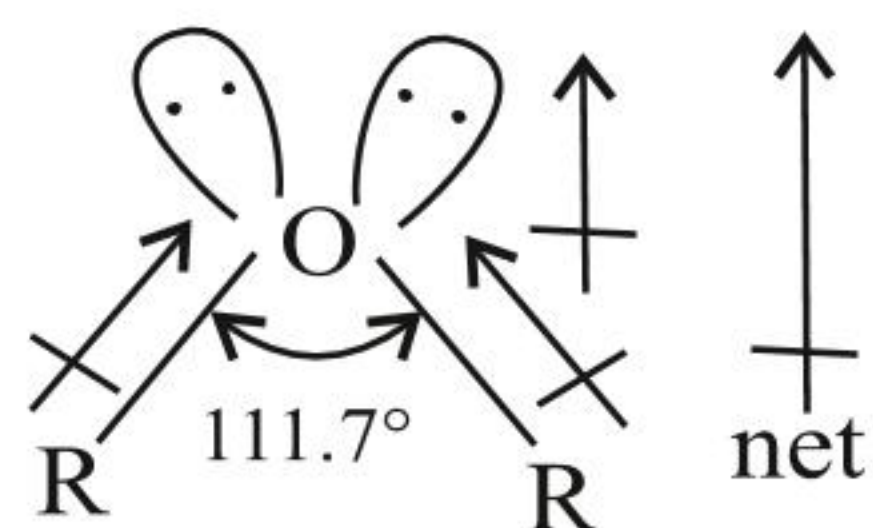


Method III is not feasible. It is a non-symmetrical ether; dehydration gives mixtures and both alkyl groups are 1°.



4.29 PHYSICAL PROPERTIES OF ETHERS

- a. Dipolar nature:** Ethers show dipole moment and thus (C—O) bonds are weakly polar.



O atom in ether is sp^3 hybridised with 2 $LP\bar{e}$'s, and (C—O—C) bond angle is 111.7° . The two dipoles do not cancel each other, hence they show dipole moments of dimethyl ether and diethyl ether which are 1.3 D and 1.18 D, respectively.

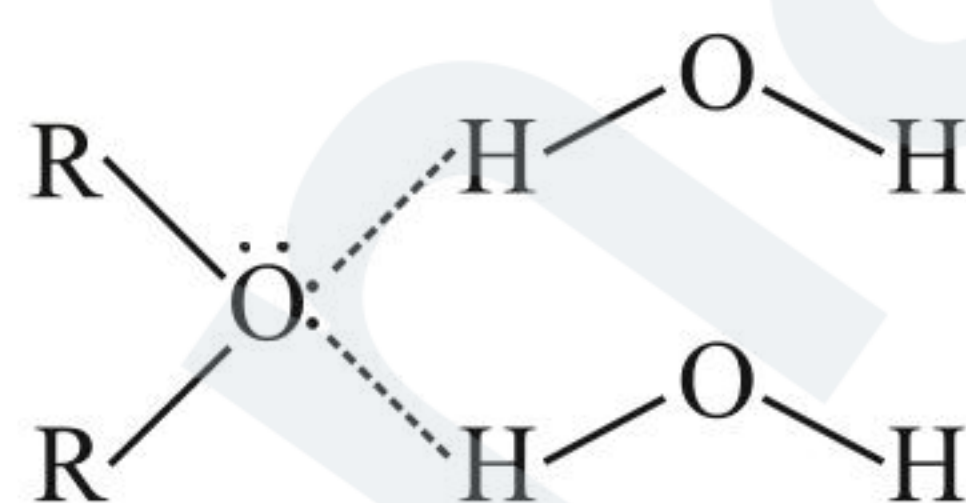
- b. Physical state, colour, and odour:** Dimethyl ether and ethyl methyl ethers are gases at ordinary temperature while the other higher homologues of ethers are colourless liquids with characteristic 'ether smell'.

- c. Boiling points:** Ethers are isomeric with monohydric alcohols but their boiling points are much lower than those of the isomeric alcohols, because unlike alcohols ethers do not form H-bonding.

The weak polarity of ethers does not appreciably affect their boiling points which are comparable to those of alkanes of comparable molecular masses. For example,

	<i>n</i> -Pentane	Ethoxy ethane
Name:	(Me—)—Me)	(C ₂ H ₅ —O—C ₂ H ₅)
b.p. (K):	309.1	307.6
	Butan-1-ol	
	(Me—)—OH)	
b.p. (K):	390.0	

- d. Solubility:** The solubility of ethers containing upto three C atoms with H₂O resembles those of alcohols of the same molecular mass. The solubility of ethoxyethane and butan-1-ol in water is almost to the same extent, i.e., 7.5 and 9 gm per 100 ml of water, respectively because like alcohols, the oxygen in ether also forms H-bonding with water molecule as shown:

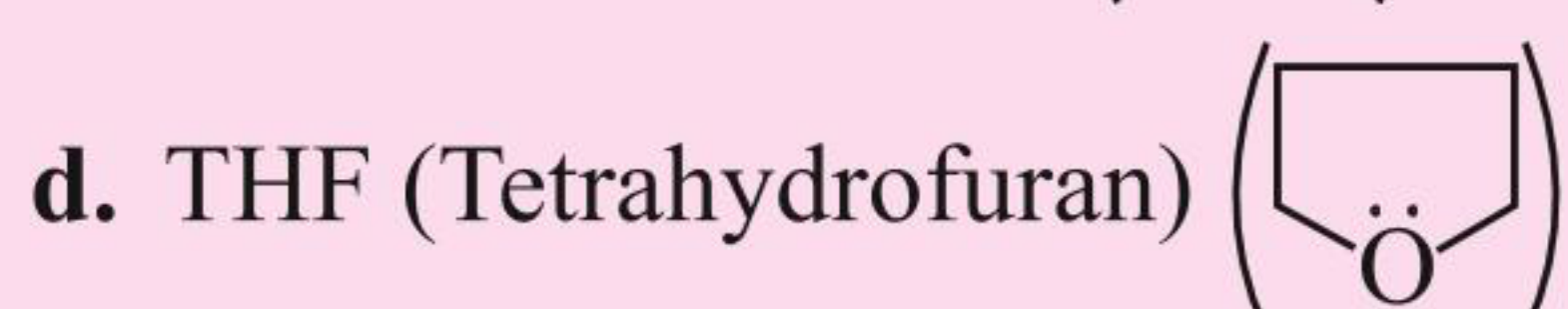
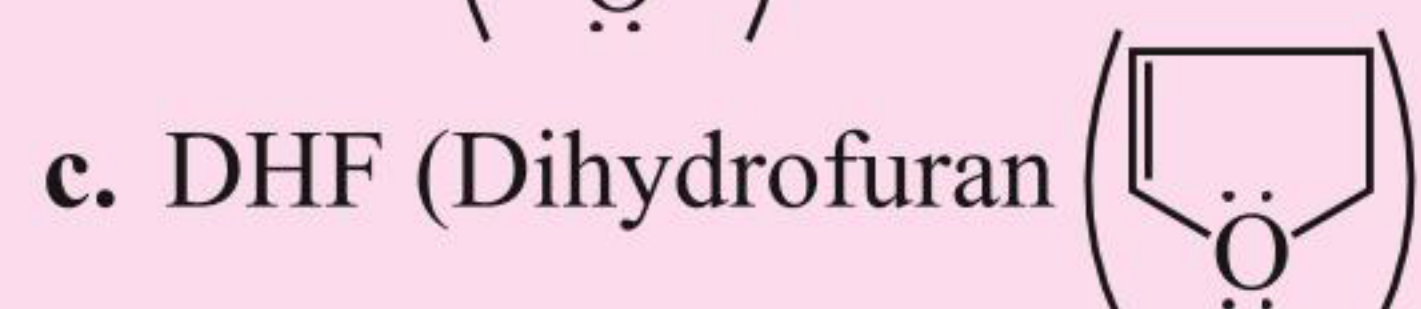


- e. Density:** All ethers are lighter than water.

ILLUSTRATION 4.21

Give the decreasing order of (i) boiling points (ii) solubilities in H₂O of the following ethers.

- a. Diethyl ether (C₂H₅—O—C₂H₅)



Sol. Boiling point:

All ethers are nearly of comparable molecular masses. The surface area is more in (a), while (b), (c), and (d) are compact molecules and have less surface area. The more the surface area, the higher is the boiling point.

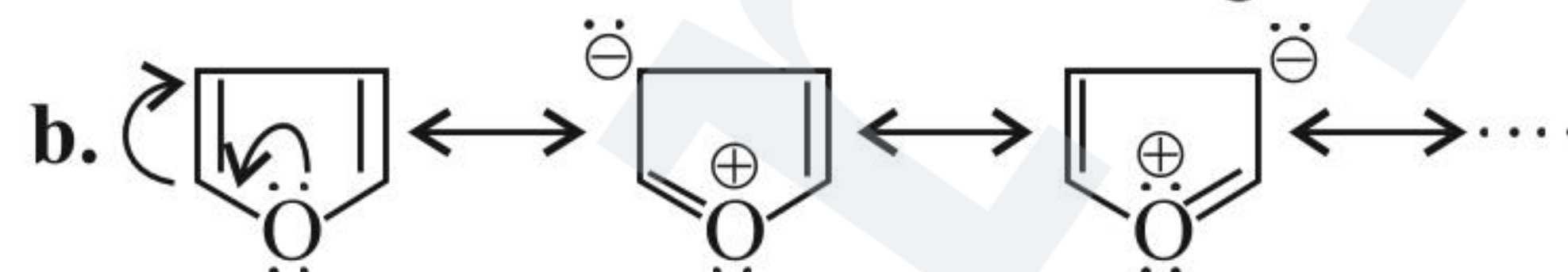
Decreasing boiling point order is: $a > d > c > b$.

(Molecular mass of $a > d > c > b$.)

Solubility:

- i. Greater the \bar{e} -density on the O atom, stronger is the H-bond and more soluble is the ether.

In (b) and (c), some \bar{e} -density on the O atom is taken away because of the extended π -bonding with the double bond.



In (b), due to more resonating structure, there is less \bar{e} density on the O atom than in (c).

- ii. The lesser the surface area, i.e., more compact and spherical, the more surface contact is available for H₂O molecule to form H-bond. The decreasing order of solubilities in H₂O is: $d > a > c > b$.

4.30 CHEMICAL REACTIONS OF ETHERS

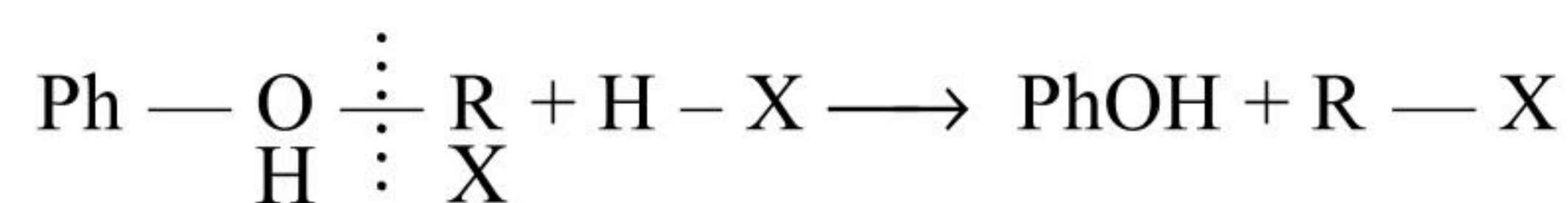
- a. Cleavage of (C—O) bond in ethers:**

Ethers are almost as inert as alkanes. Under ordinary conditions, they are stable to dilute acids, bases, catalytic hydrogenation, as well as to most other reducing agents because the functional group ($-\ddot{O}-$) does not have any active site as compared to ($-\text{OH}$) groups of alcohols and phenols even though O atom in both these functional groups has 2 LP of \bar{e} 's.

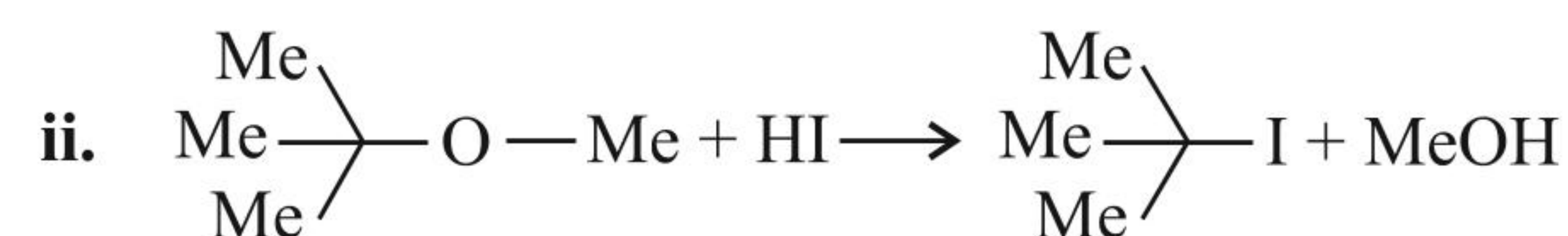
The cleavage of (C—O) bond in ethers takes place under drastic conditions with excess of HX, i.e., with conc. HI or HBr at high temperature (373 K).



- b. Alkyl aryl ethers are cleaved at the ($R-\ddot{O}$) bond because (Ar—O) bond is more stable, for example,

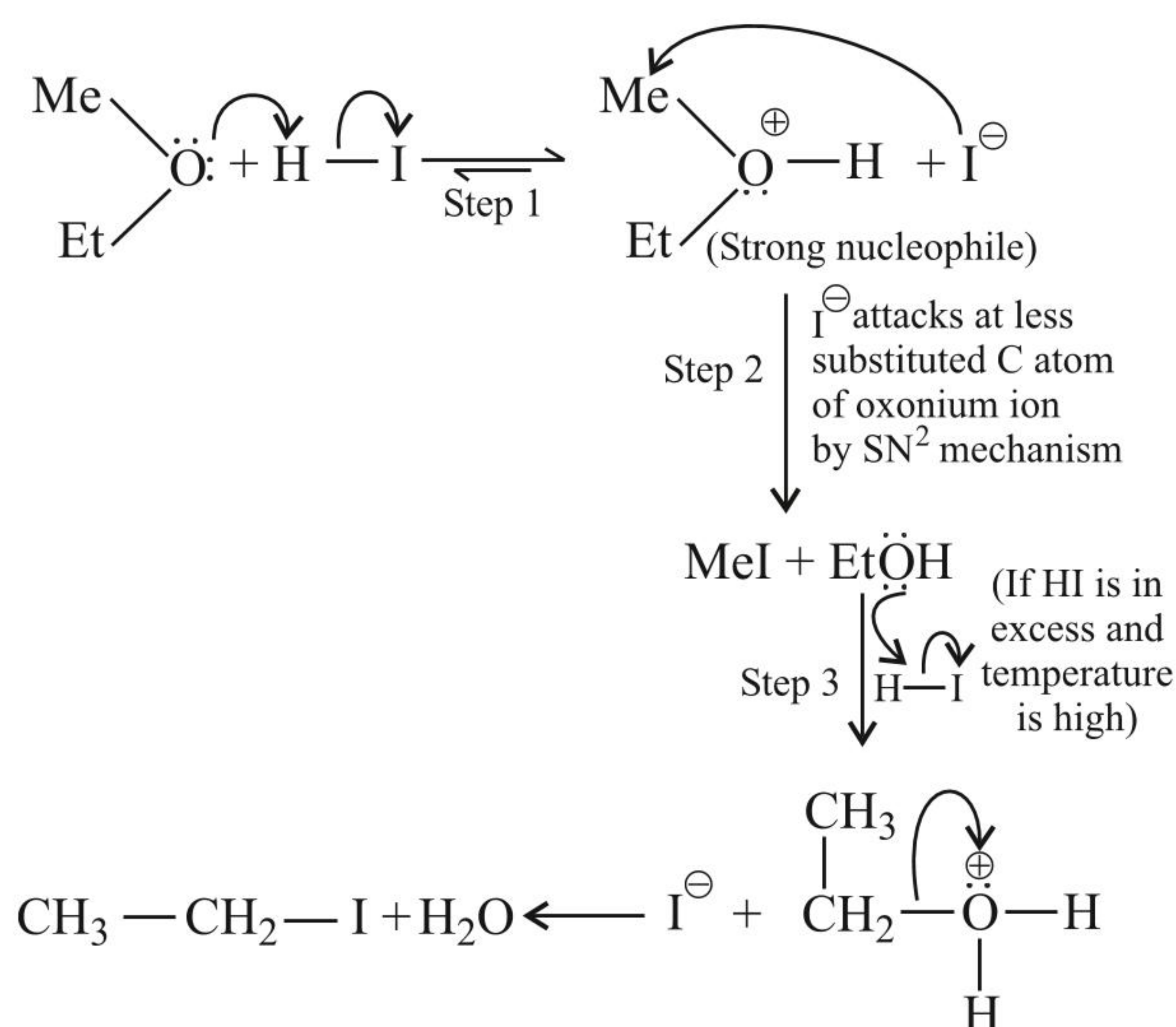


- c. When ethers with two different 1° alkyl groups are cleaved, the halide formed is with smaller alkyl group. When one of the (R—) groups is 3°, the halide formed is 3° RI, for example,



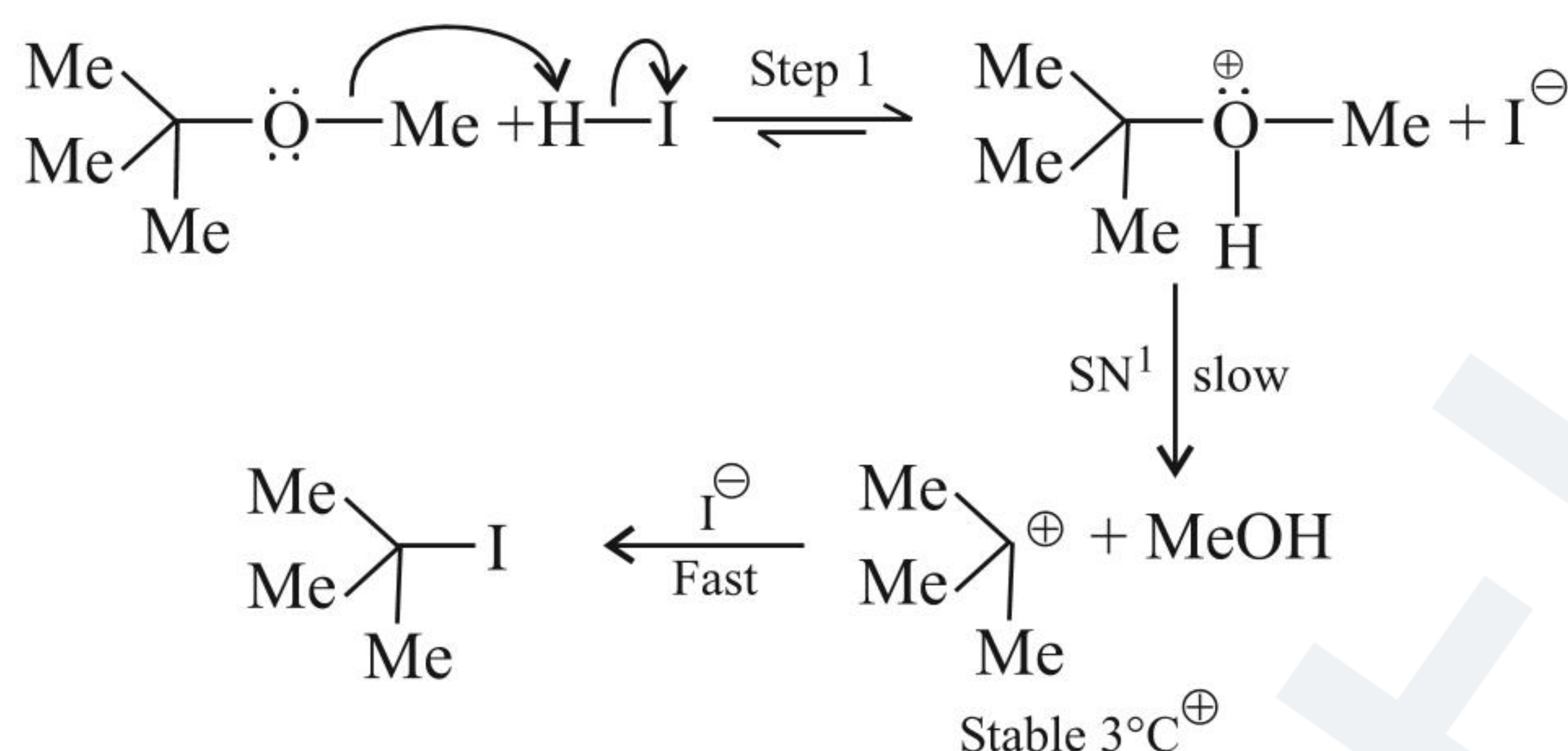
4.30.1 MECHANISM (WHEN BOTH ALKYL GROUPS ARE 1°, THE HALIDE FORMED IS WITH SMALLER ALKYL GROUP)

The cleavage of ethers takes place with conc. HI or HBr because these reagents are sufficiently acidic.



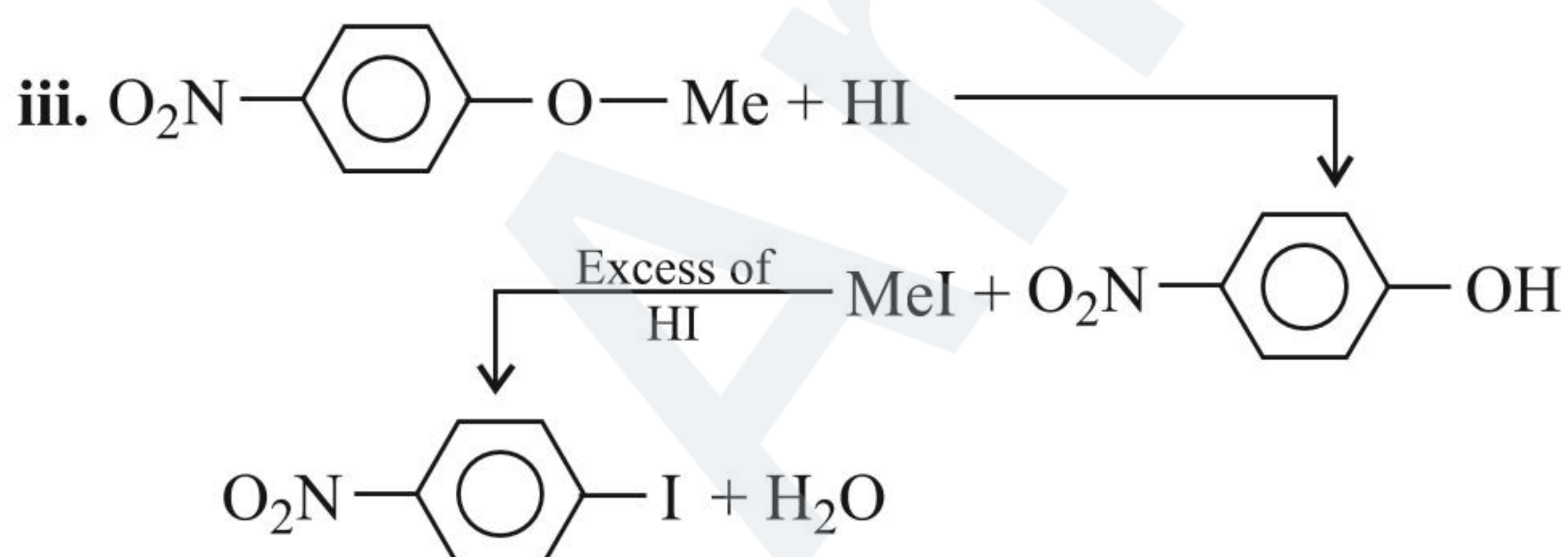
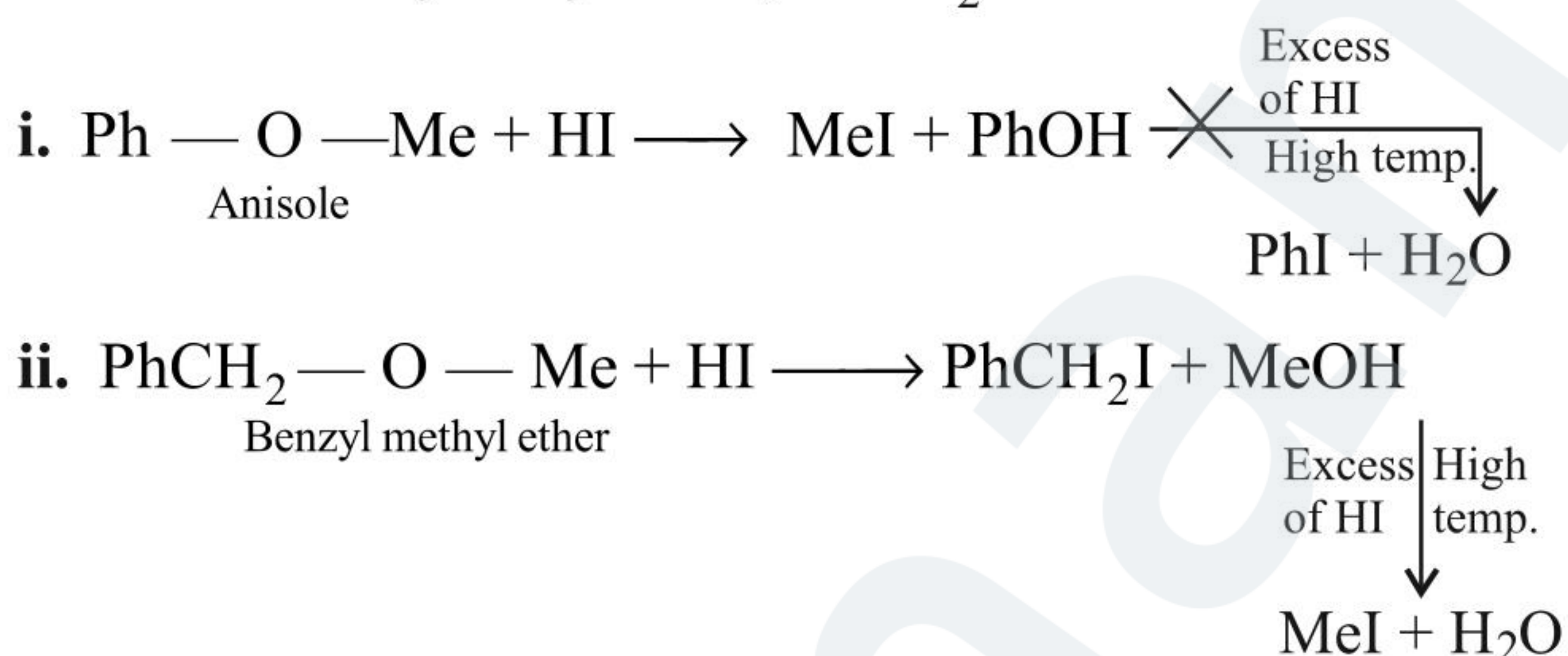
4.30.2 MECHANISM WHEN ONE OF THE ALKYL GROUPS IS 3°

The halide formed is 3° RI because in step 2 of the reaction, the departure of leaving group (CH_3-OH) produces more stable 3° C^+ and the reaction follows $\text{S}_{\text{N}}1$ mechanism, for example,



In case of aryl alkyl ether, RI and ArOH are formed.

In case of benzyl alkyl ether, PhCH_2I and ROH are formed.

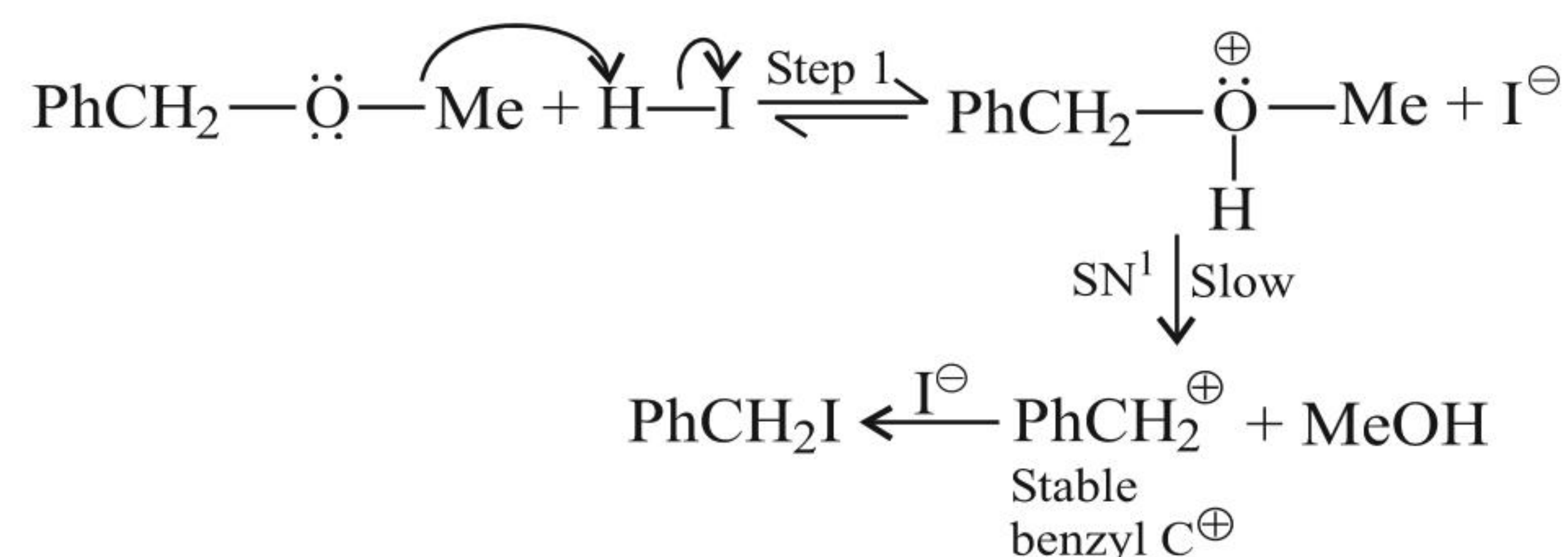
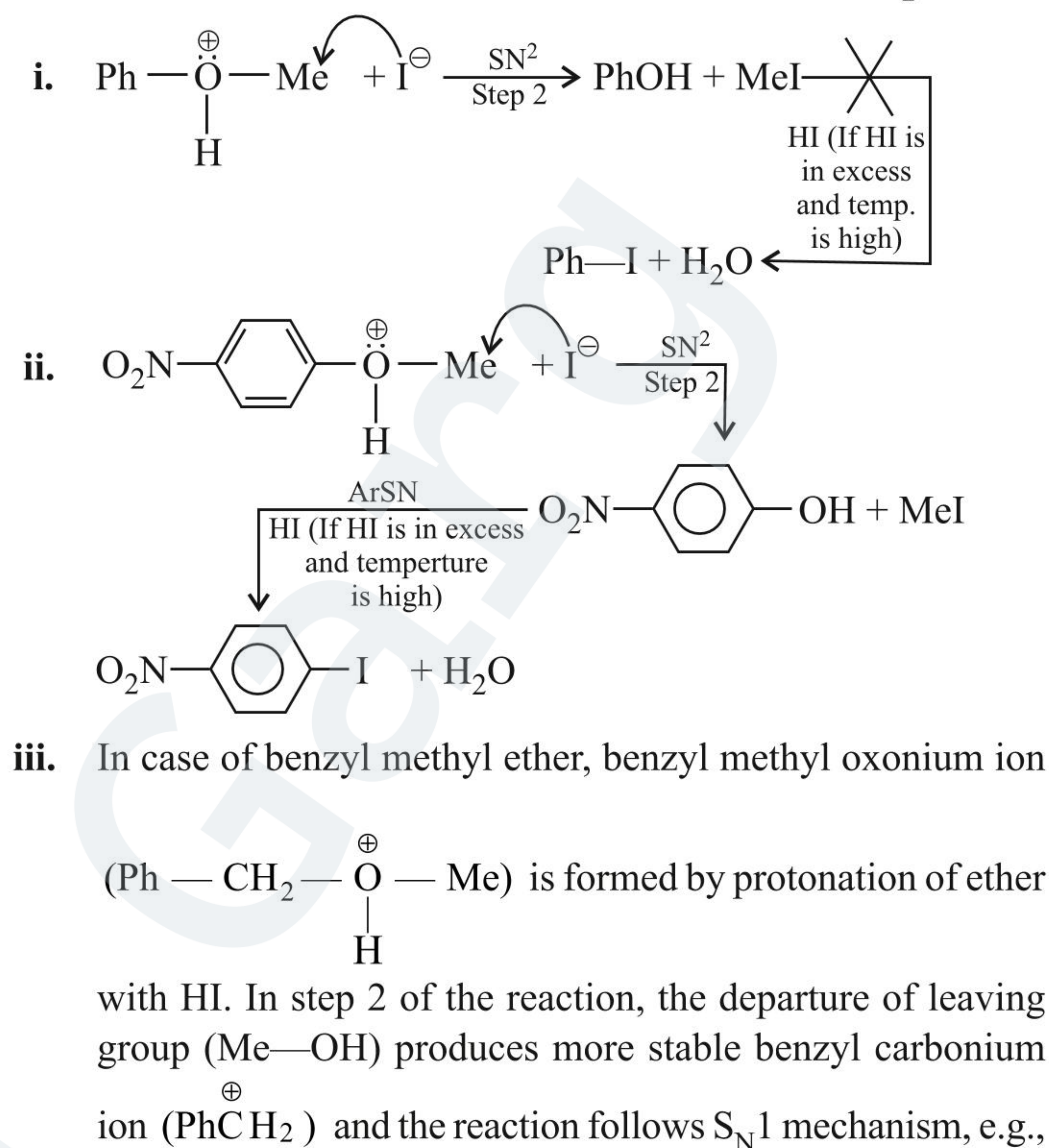


4.30.3 MECHANISM IN CASE OF ANISOLE

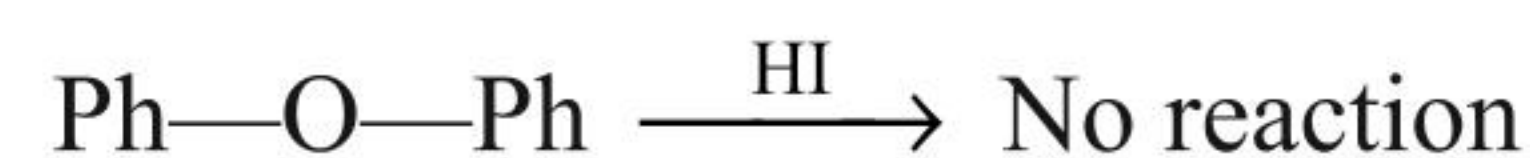
Methyl phenyloxonium ion ($\text{Ph}-\text{O}^+-\text{Me}$) is formed by

protonation of ether with HI. The ($\text{Me}-\text{O}$) bond is weaker than ($\text{Ph}-\text{O}$) bond because the ($\text{C}-$) of phenyl group is sp^2 -hybridised and there is partial double bond character due to resonance. Therefore, I^- attacks (Me) group and breaks ($\text{Me}-\text{O}$) bond to

form MeI and PhOH. Phenols do not react further with HI to form PhI because the sp^2 -hybridised ($\text{C}-$) of phenol does not undergo ArSN reaction unless it is activated by EWG (e.g., (NO_2) group.

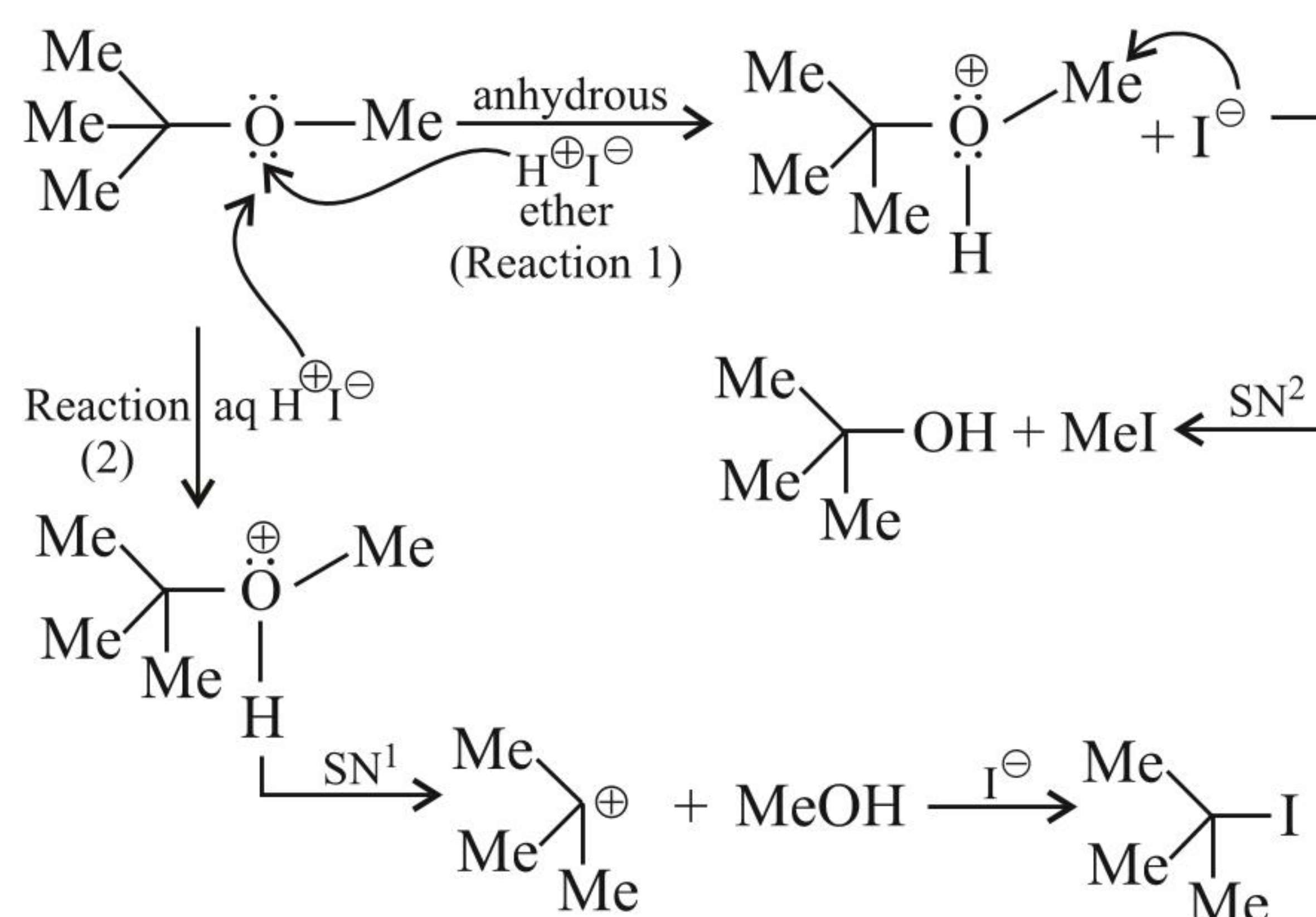


Reaction of diaryl ethers with HI: Diphenyl ether is not cleaved by HI.



4.31 REACTION OF ETHER BY AQUEOUS HI AND ANHYDROUS HI

t-Butyl methyl ether with aqueous or conc. HI undergoes cleavage by $\text{S}_{\text{N}}1$ mechanism and with anhydrous HI/ether, cleavage takes place by $\text{S}_{\text{N}}2$ mechanism, e.g.,

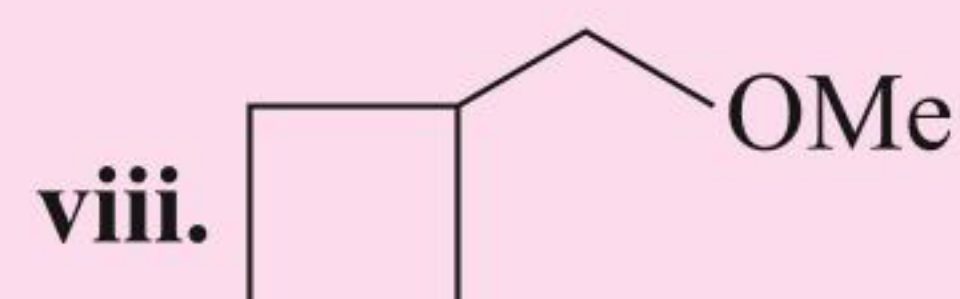
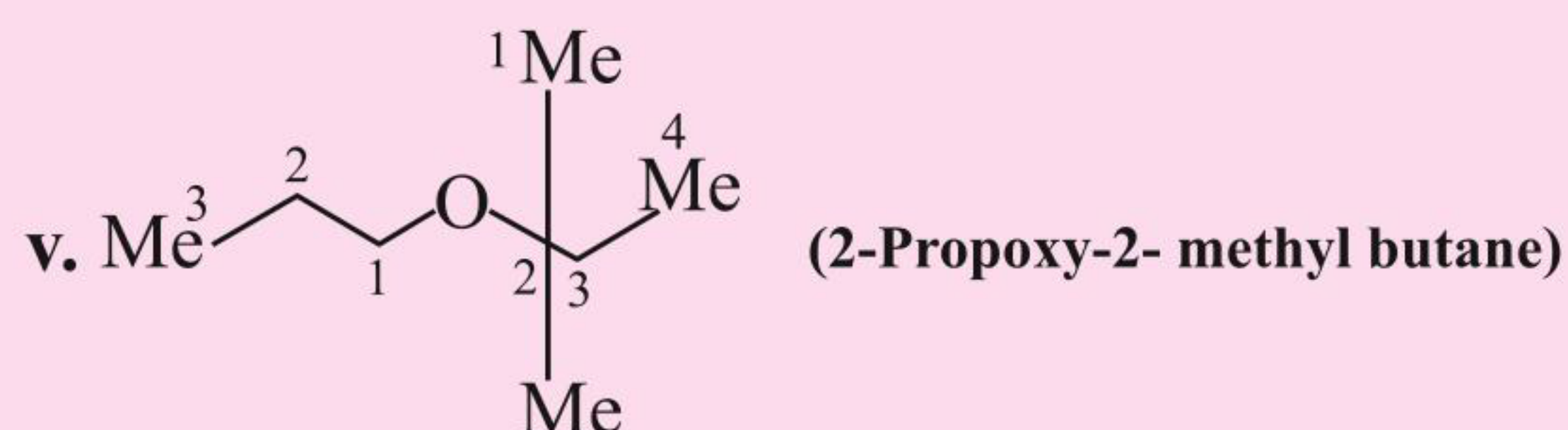
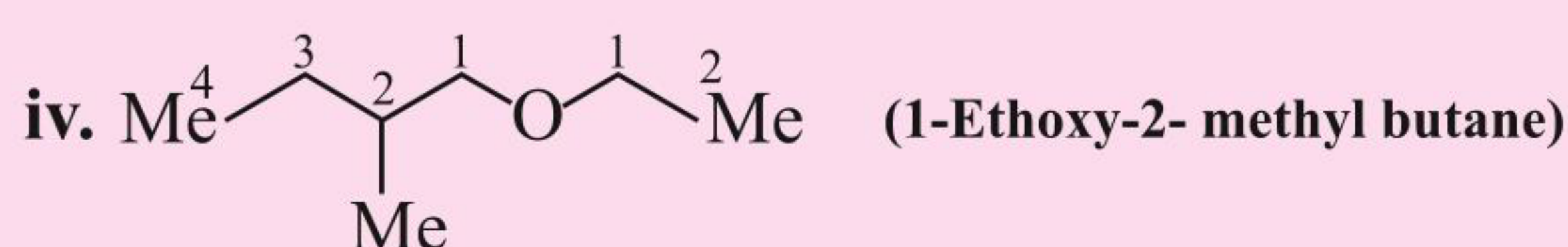
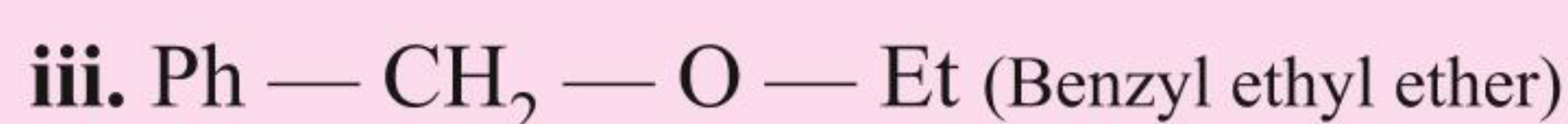
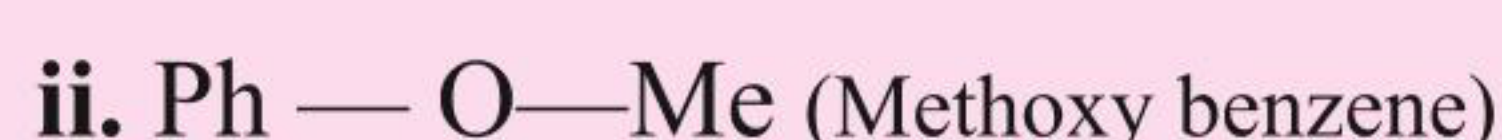
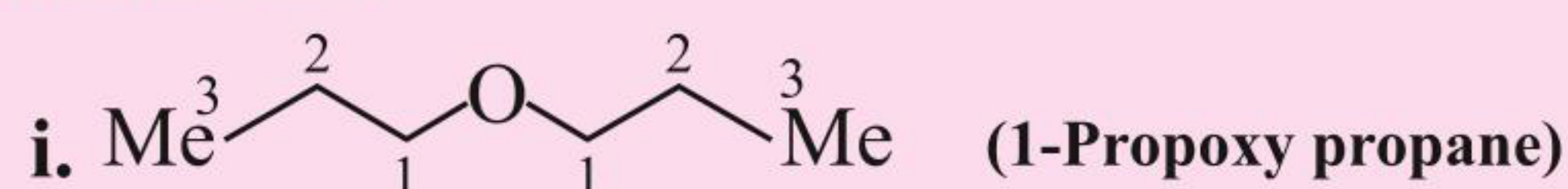


The low polarity of solvent (ether) in reaction (1) favours S_N2 mechanism and the nucleophile I^- attacks the $1^\circ C$ of (Me) group.

The high polarity of solvent (H_2O) in reaction (2) favours an S_N1 mechanism giving the $3^\circ C^+$, and the nucleophile I^- attacks the $3^\circ C^+$ of (Me_3C-) group.

ILLUSTRATION 4.22

a. Give the major products formed by heating the following ethers with conc. HI with mentioning S_N1 or S_N2 mechanism.



b. Give the products of the above ethers with excess of HI.

c. Why does S_N2 cleavage occur at a faster rate with HI than with HCl?

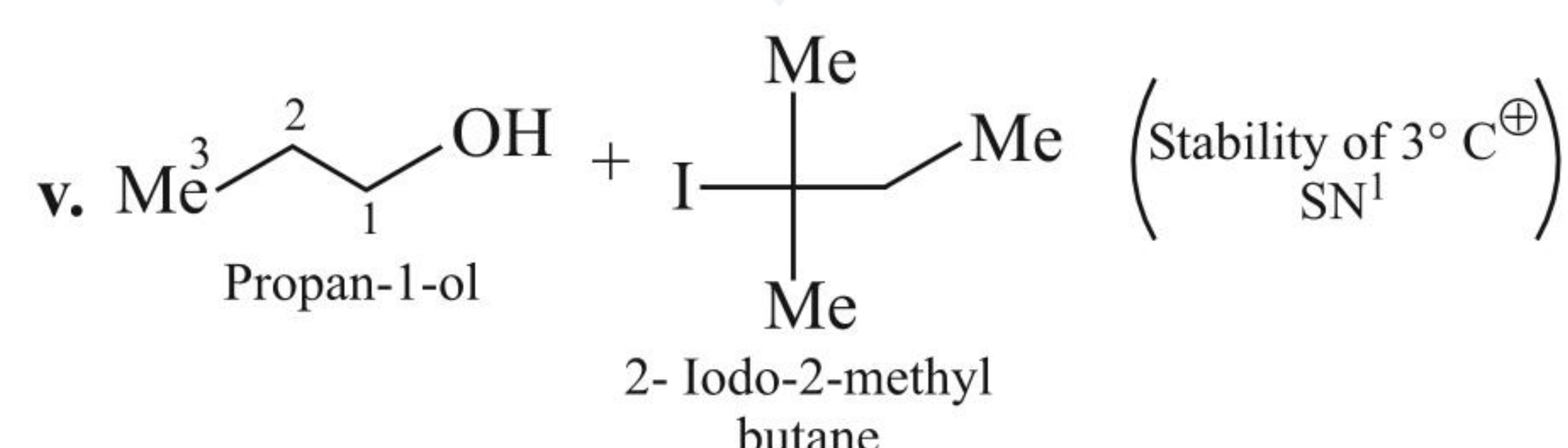
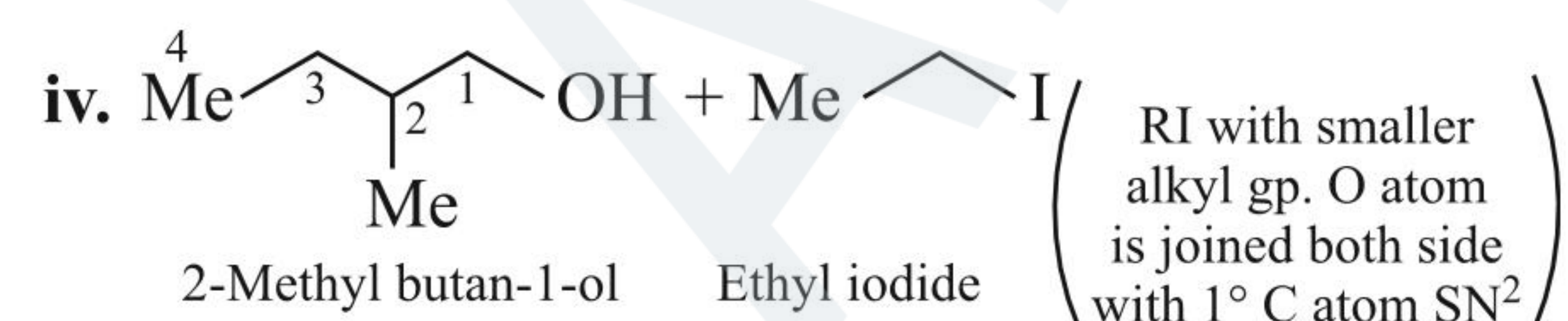
Sol.

a. i. Symmetrical ether $1^\circ R$ groups, S_N2

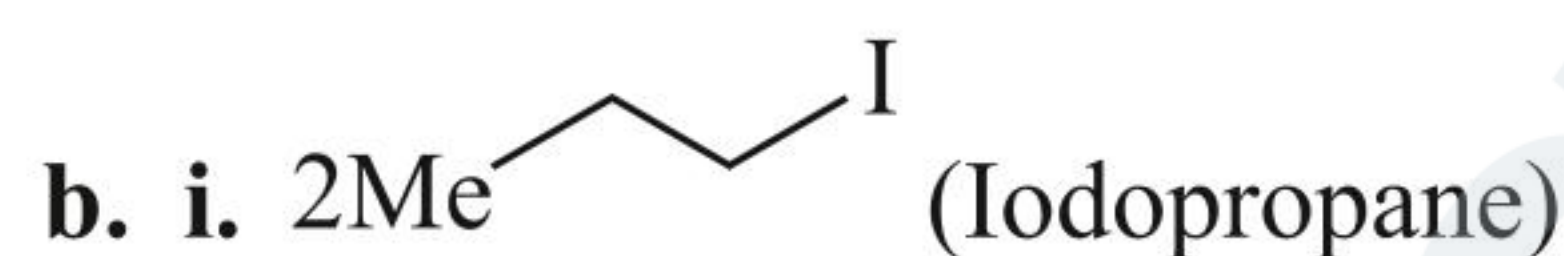
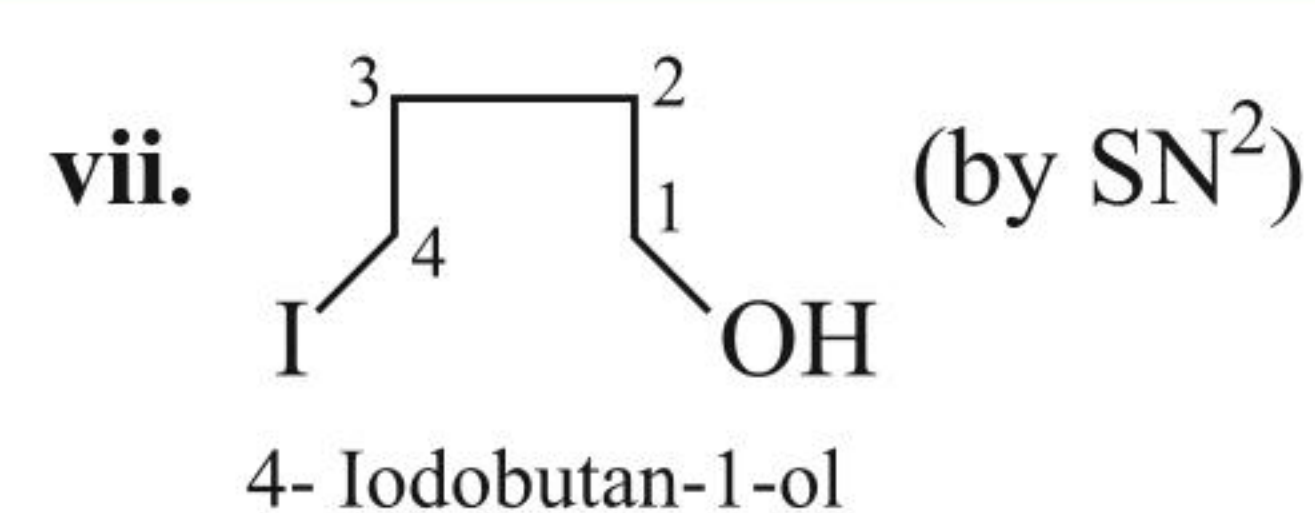


ii. Phenol ($Ph-OH$) + MeI (S_N2) ($1^\circ R$ groups)

iii. $PhCH_2I + EtOH$ (Stability of benzyl C^+) (S_N1)
Benzyl iodide Ethanol

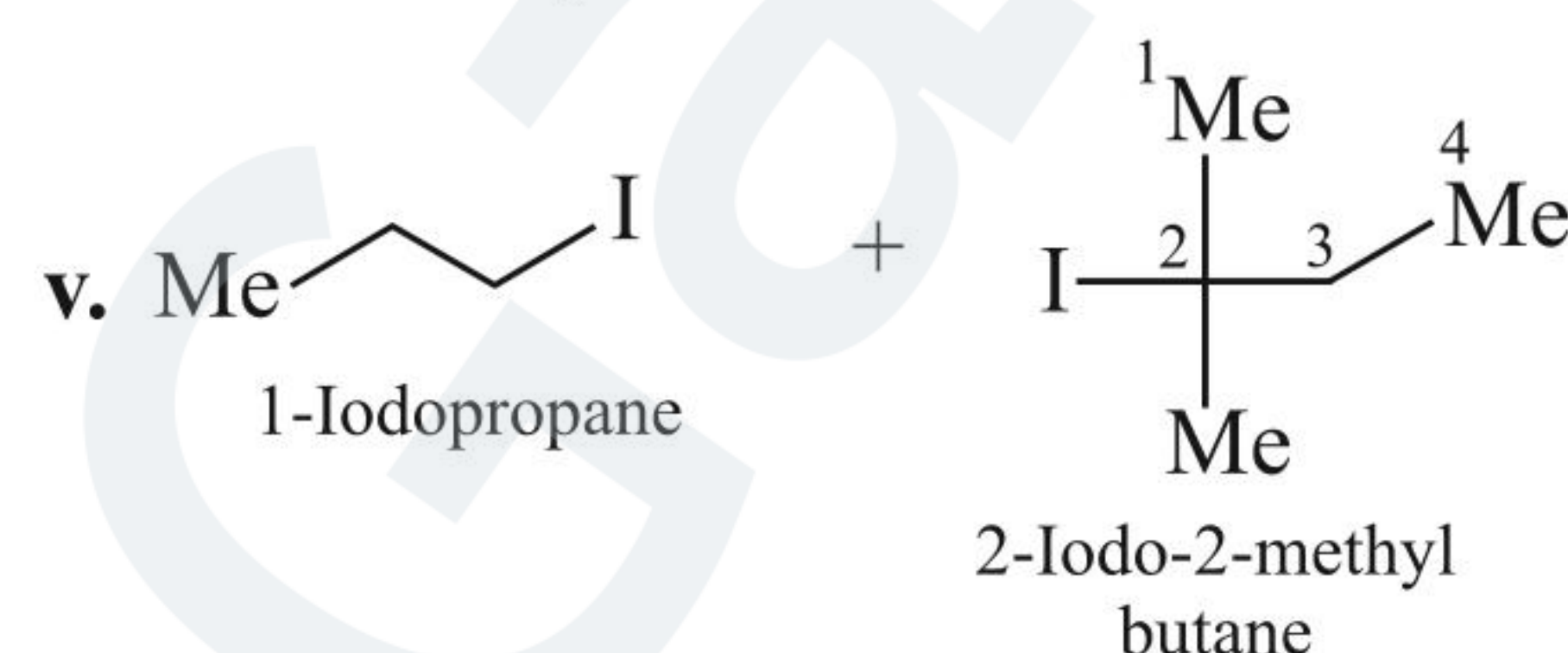
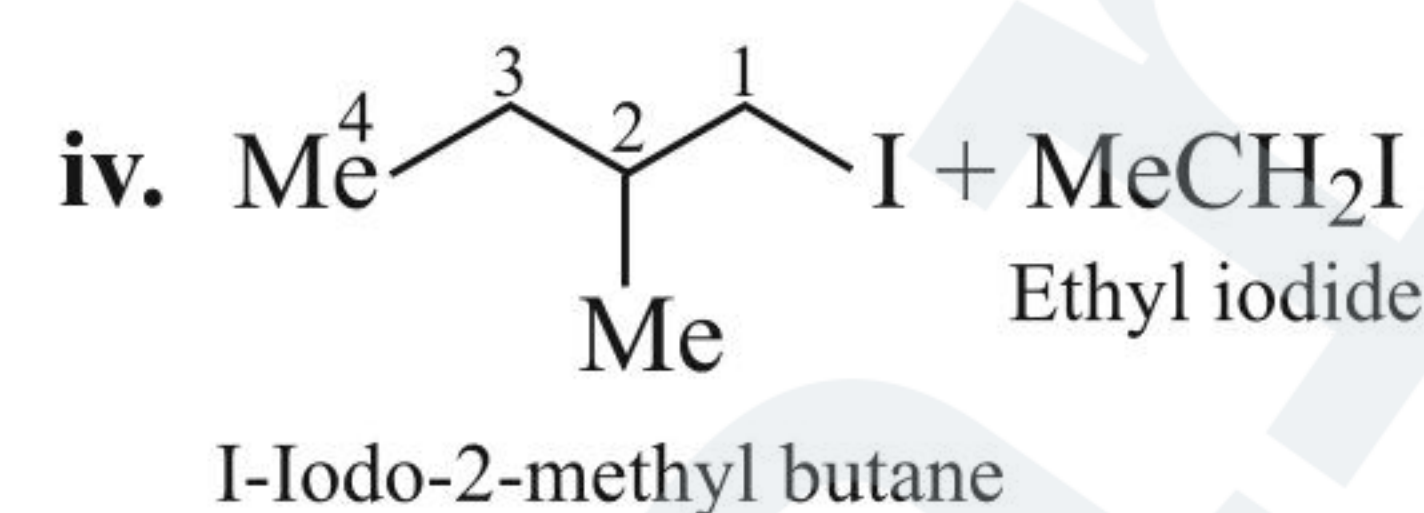


vi. $PhCH_2I + PhOH$ (Stability of benzyl C^+ S_N1)
Benzyl iodide Phenol

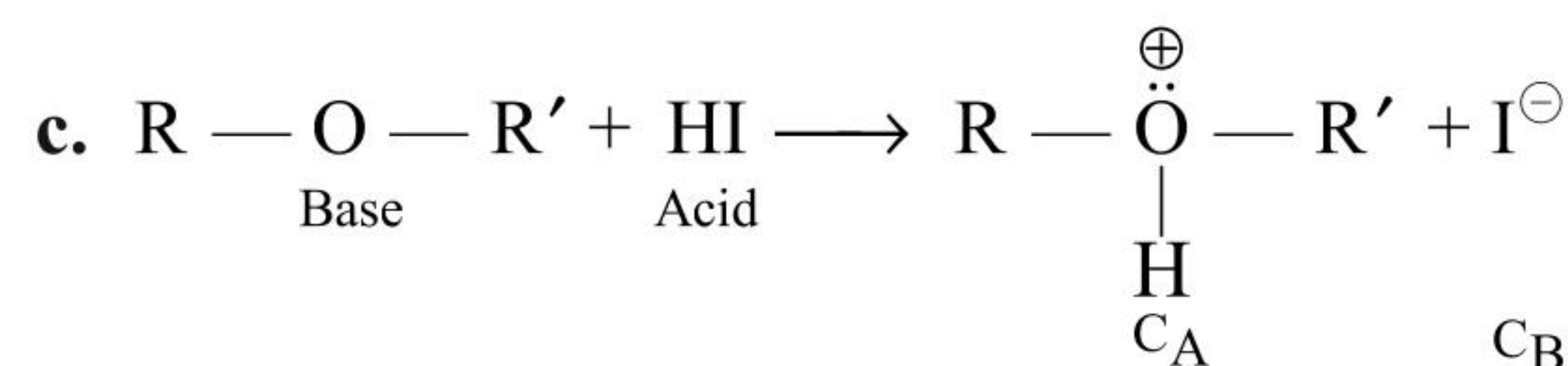
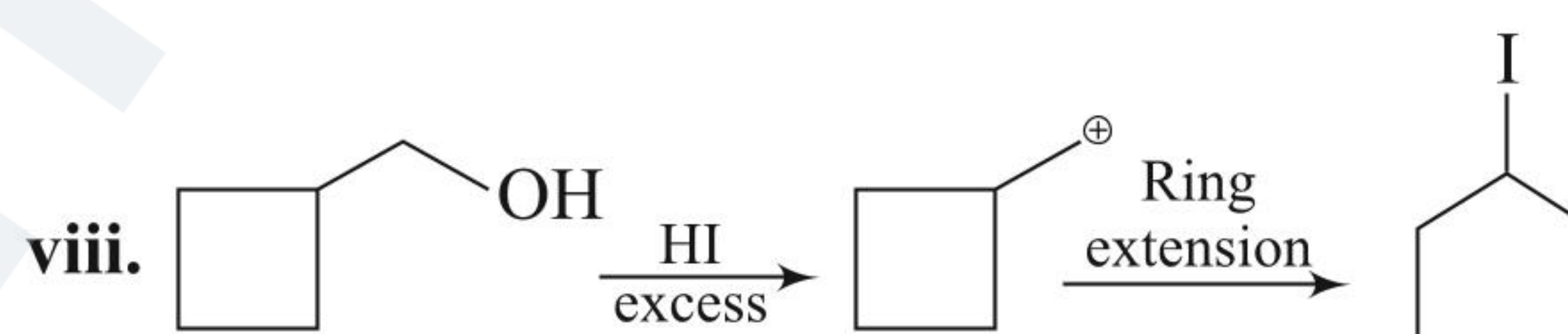
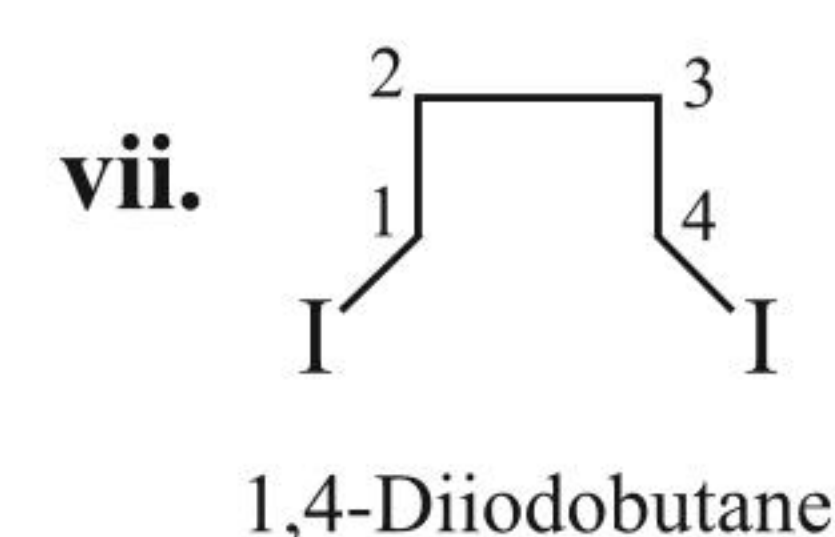


ii. $PhOH + MeI$ ($PhOH$ does not undergo $ArSN$ reaction unless activated by EWG)

iii. $PhCH_2I + EtI$ (Benzyl iodide + Ethyl iodide)



vi. $PhCH_2I + PhOH$
Phenol doesn't undergo $ArSN$ reactions.



The transfer of H^+ to ROR' is greater with HI, which is a stronger acid, than with HCl. Moreover, I^- being a better nucleophile than Cl^- , it reacts at faster rate in step 2 of the mechanism of the reaction.

4.32 FORMATION OF COORDINATION COMPLEXES

Ethers act as Lewis bases because of the presence of 2 $LP\bar{e}$'s and are capable of reacting with Lewis acids such as BF_3 , $AlCl_3$, $FeCl_3$, $RMgX$ to form coordinate complexes known as etherate.

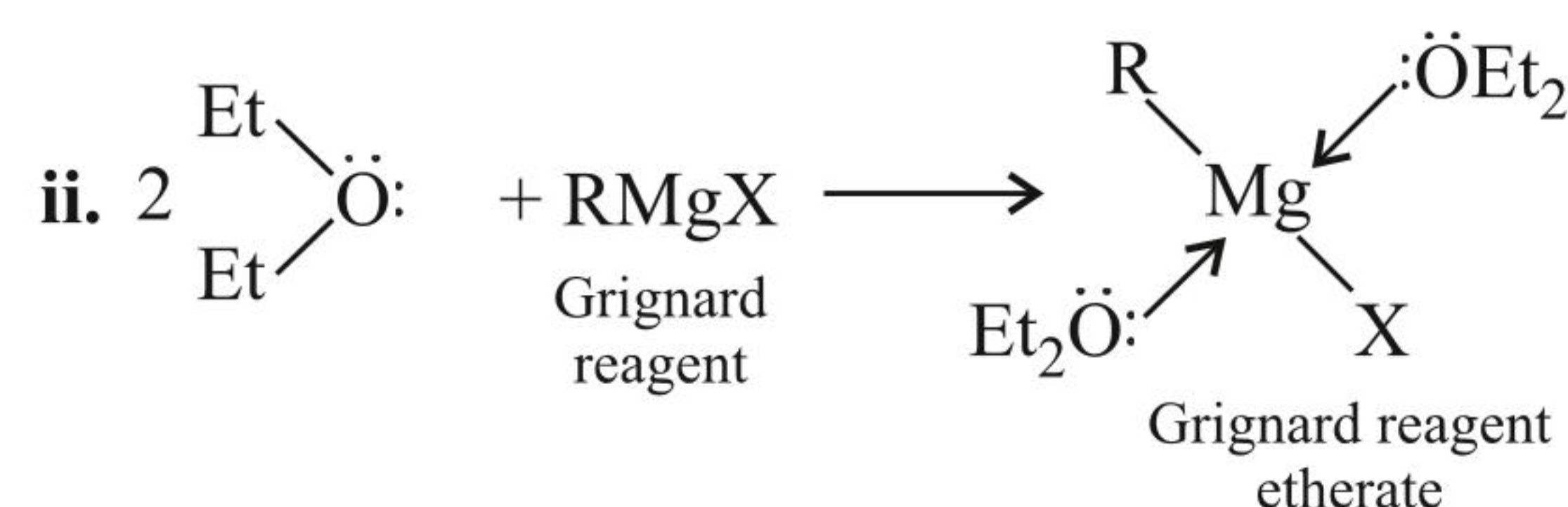
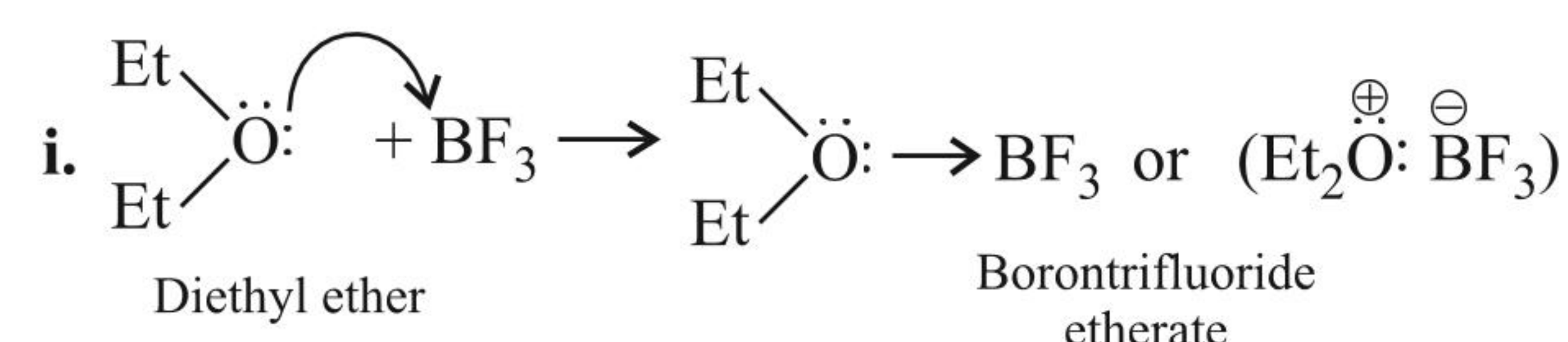
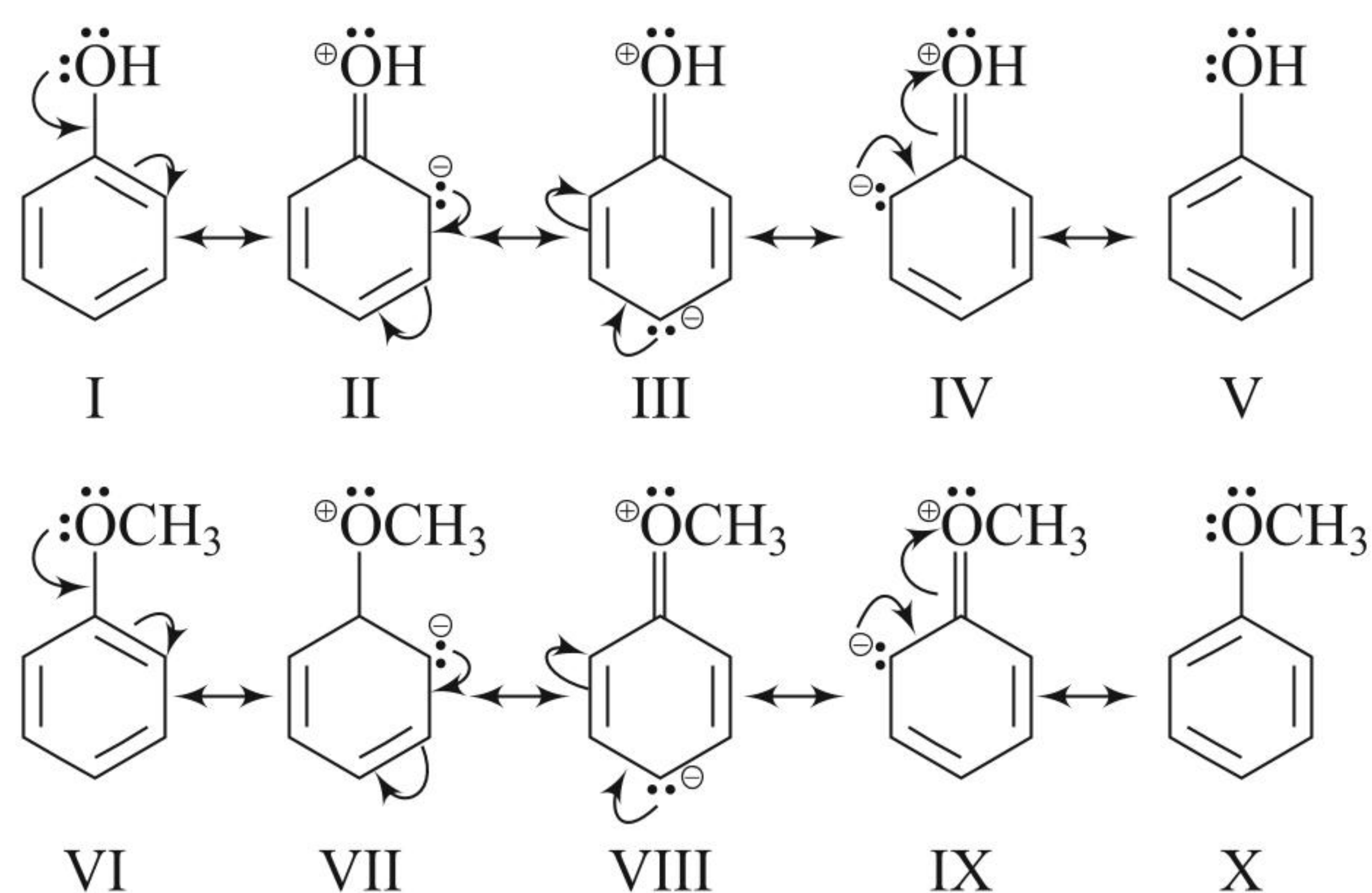


ILLUSTRATION 4.23

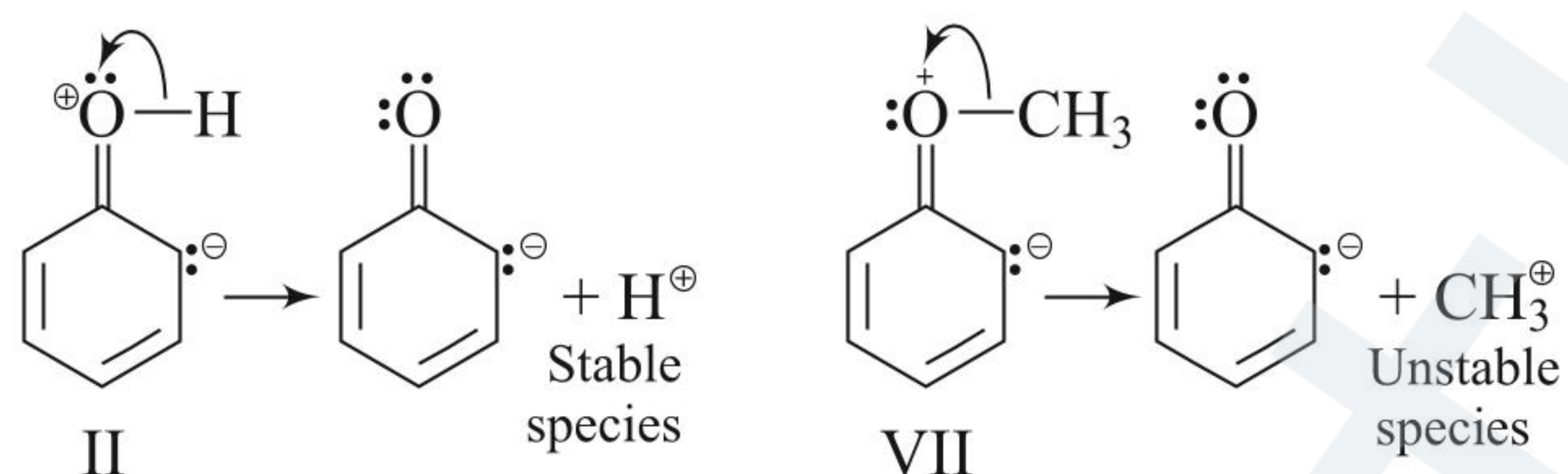
Explain why anisole is less reactive than phenol towards electrophilic substitution (SE) reactions.

Sol. Both —OH and —OCH₃ have +R-effect as shown below:



Structures (II to IV) involve separation of +ve and -ve charges. Similarly, structure (VII-IX) involve separation of +ve and -ve charges. But structure (II to IV) can stabilize themselves by releasing a proton which is a very stable chemical species

In contrast, structure (VII-IX) cannot stabilize themselves by releasing a methyl carbocation which is very unstable chemical species.



It is because of this extra stability of structures, II-IV through loss of a proton which is responsible for greater reactivity of phenol over anisole.

4.33 ZEISEL METHOD FOR THE DETERMINATION OF METHOXY GROUPS

The reaction of HI with ethers forms the basis of Zeisel method for the estimation of alkoxy groups such as methoxyl group (—OCH₃) and ethoxyl (—OC₂H₅) group. The alkyl iodide (CH₃I or C₂H₅I) produced as a result of action of HI is absorbed in ethanolic AgNO₃ solution and AgI thus formed is weighed; for example, 1.34 gm of a compound (A) gave 7.04 gm of AgI by Zeisel's method for the determination of methoxyl groups. The compound (A) (mol. wt. = 134) contains how many methoxyl groups?

Ans. 1.34 gm of (A) gave 7.04 gm of AgI. (Molecular mass of AgI = 108 + 127 = 235).

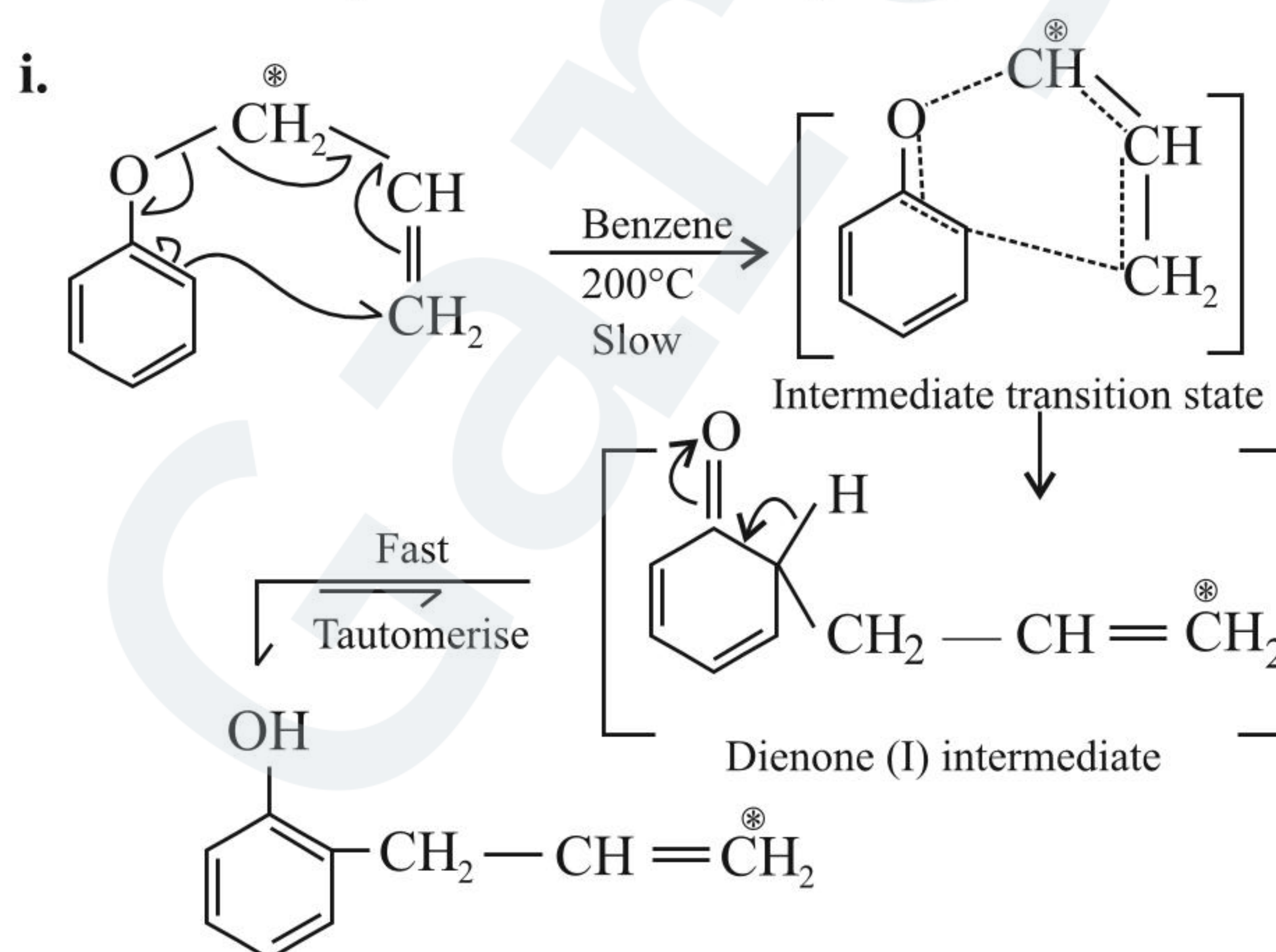
$$\begin{aligned} \therefore 1.34 \text{ gm of (A) gave} &= \frac{7.04}{1.34} \times 134 = 704 \text{ gm of AgI} \\ &= \frac{704}{235} \approx 3 \text{ mol of AgI} \\ &= 3 \text{ mol of (—OCH}_3\text{) group.} \end{aligned}$$

4.34 CLAISEN REARRANGEMENT REACTION

On heating aryl allyl or alkyl allyl ethers in inert solvent (e.g., benzene), the allyl group migrates from the *ortho* position to the ring, preferably at *ortho* position, but *para* if the *ortho* position is blocked.

4.34.1 MECHANISM

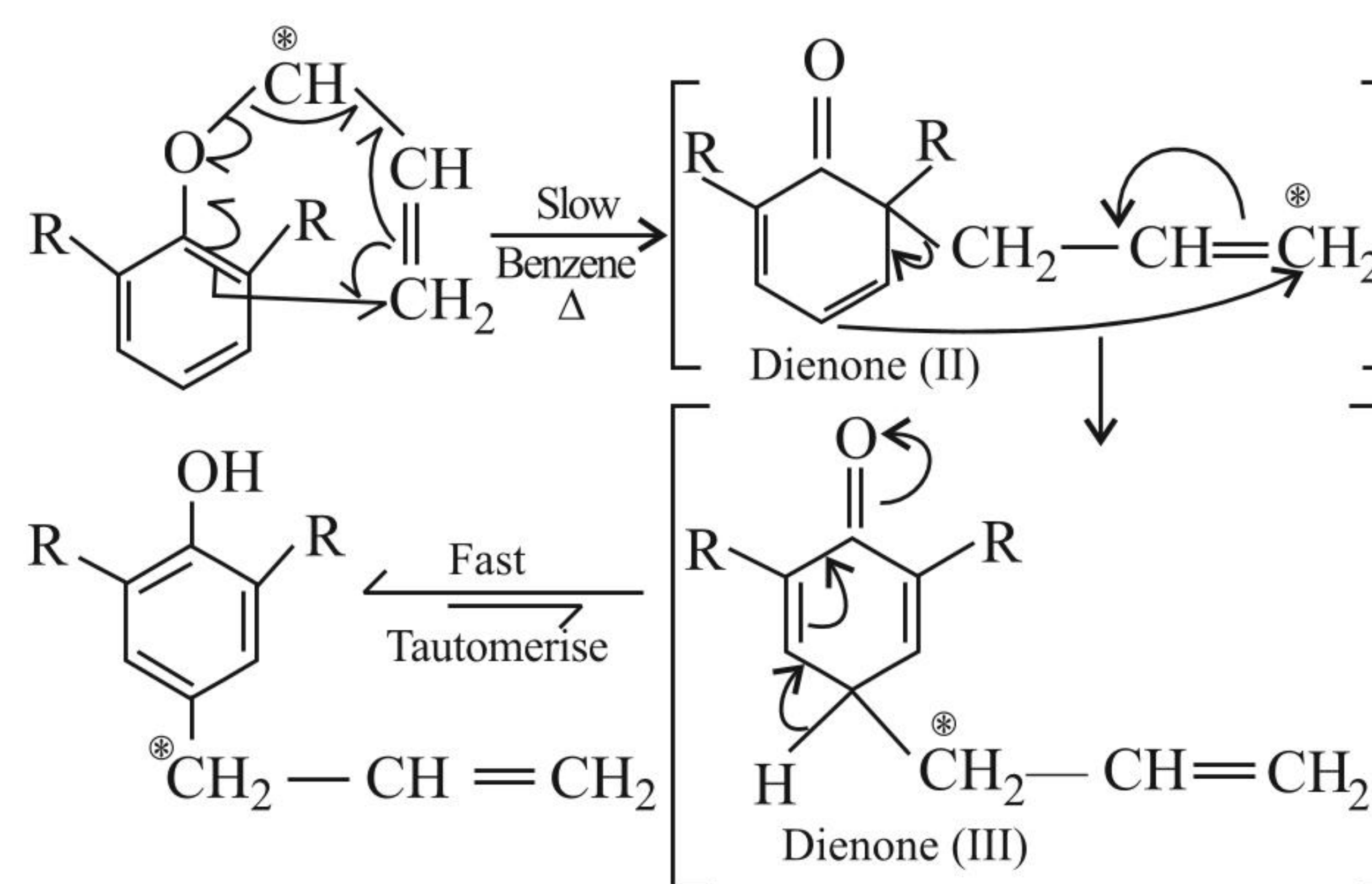
It takes place by concerted mechanism, i.e., breaking and formation of bond takes place simultaneously, e.g.,



The cyclohexadienone (I) intermediate is rapidly converted into phenolic compound for reasons of aromatic stability.

4.34.2 *para*-MIGRATION

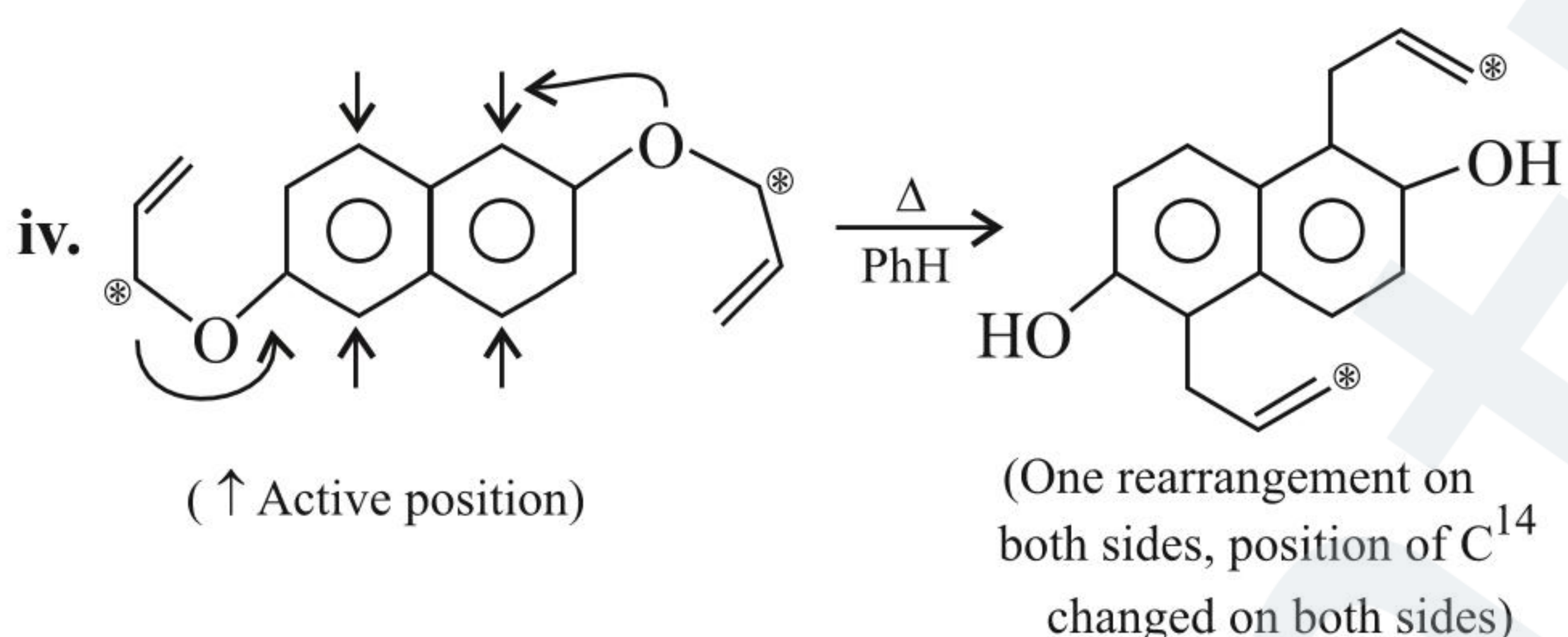
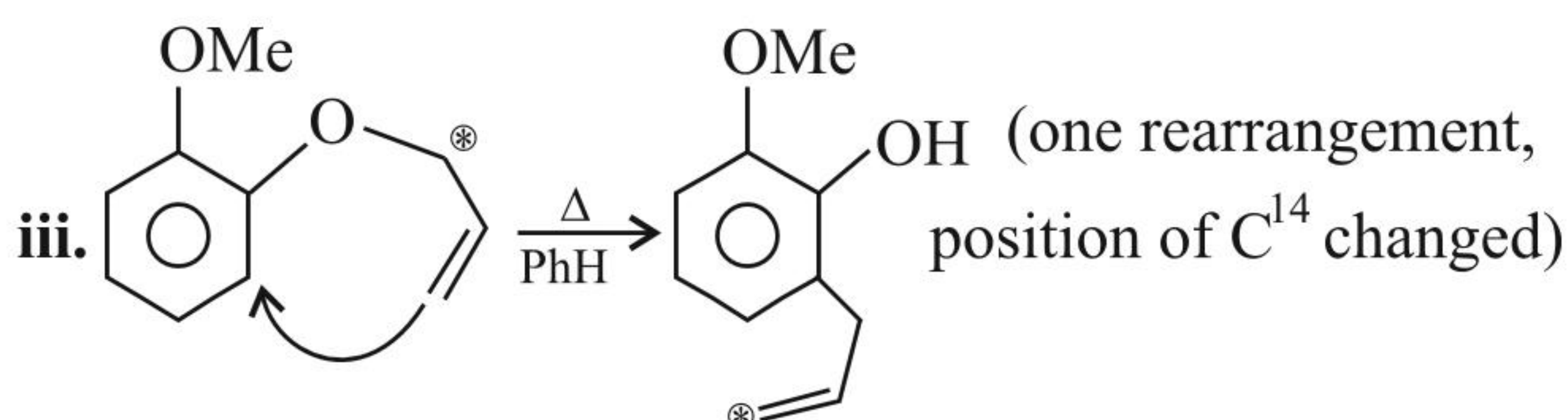
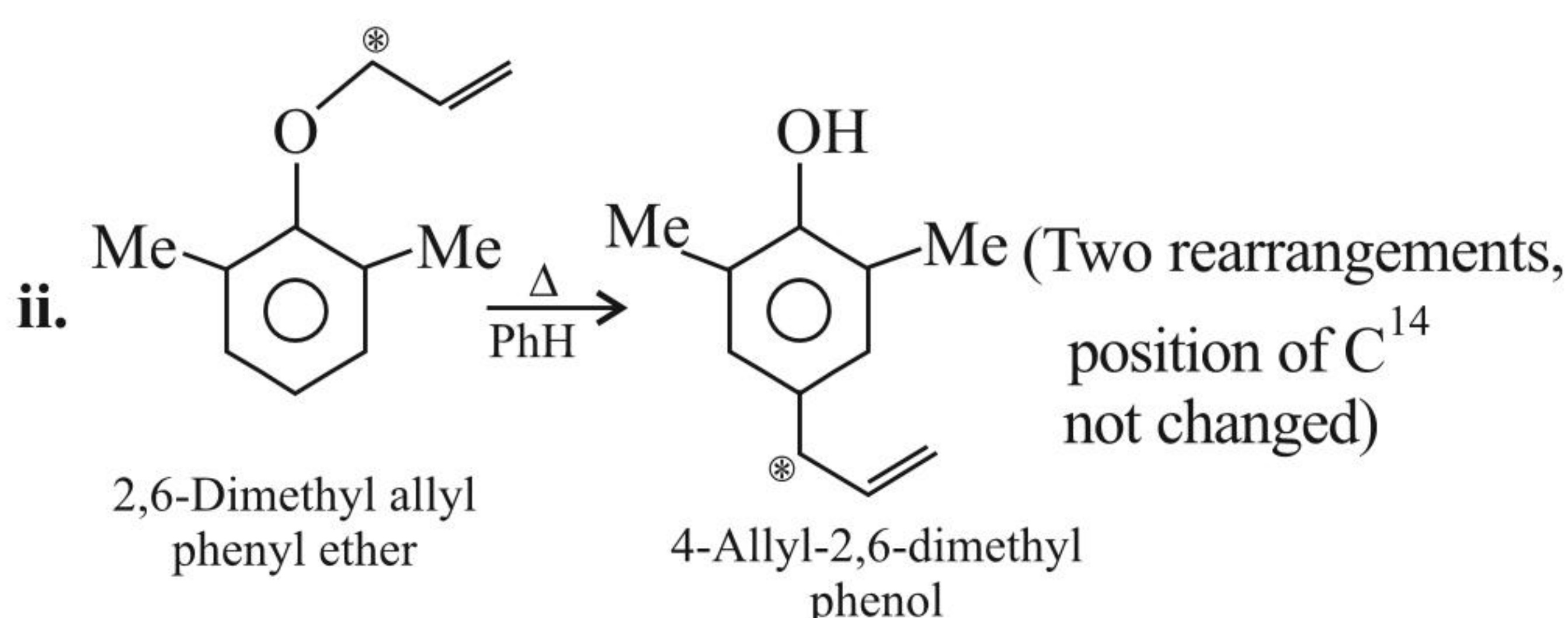
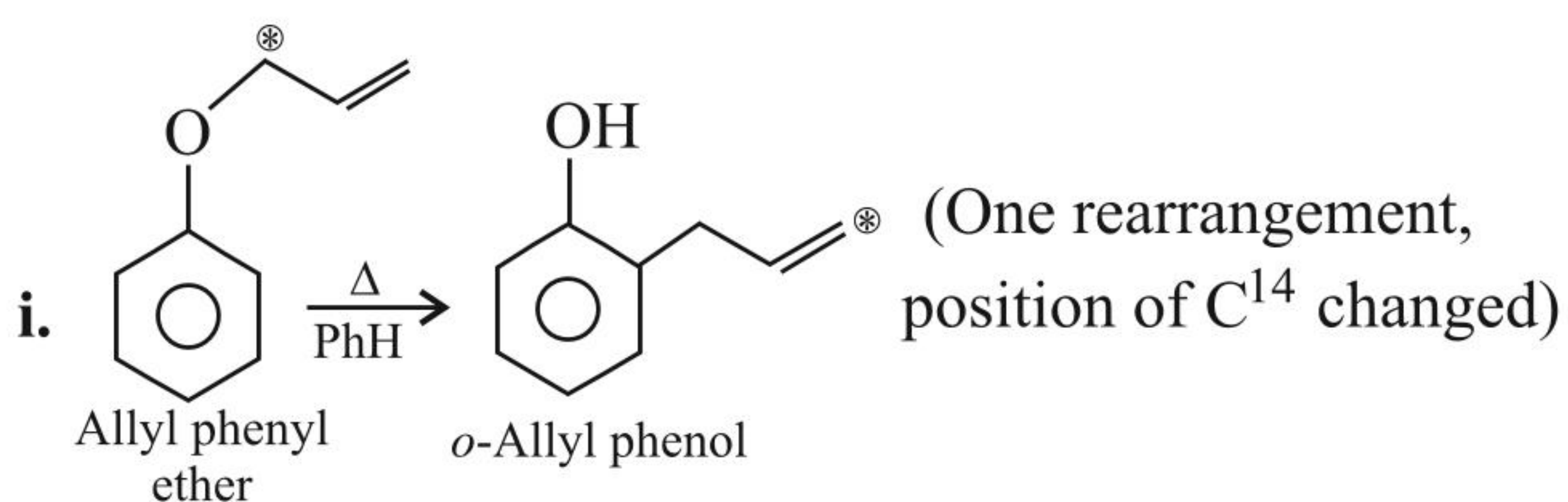
Even when *ortho* positions are substituted, the migration still occurs at the *ortho* position to form *ortho*-substituted dienone (II). However, the absence of hydrogen at the *ortho* position prevents enolisation, i.e., aromatisation. Hence, the allyl group undergoes a second migration through a similar cyclic transition state to form dienone (III) which aromatises to a phenolic compound with allyl group at Position 4.



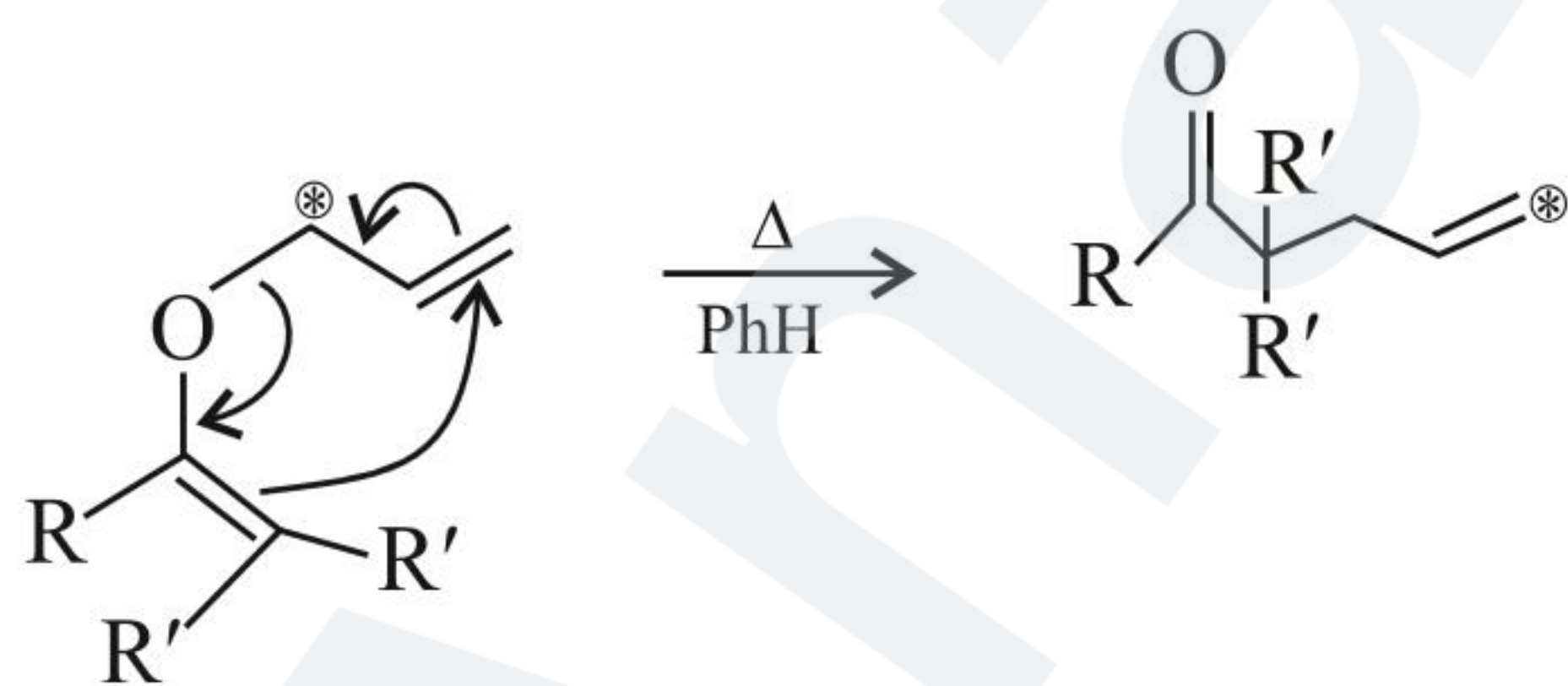
Since allyl group undergoes double inversion, it is not rearranged in the final product. This has been confirmed by isotopically labelled carbon.

There is enough evidence in support of this mechanism. The double inversion of the allyl group is proved by trapping the dienone intermediate with maleic anhydride in a Diels-Alder reaction. Further, the dienone (II) prepared separately was found to give rapidly the *para*-product on heating.

The reaction rate is unaffected by the presence or absence of substituents in the aromatic ring, since the reaction is not ionic.

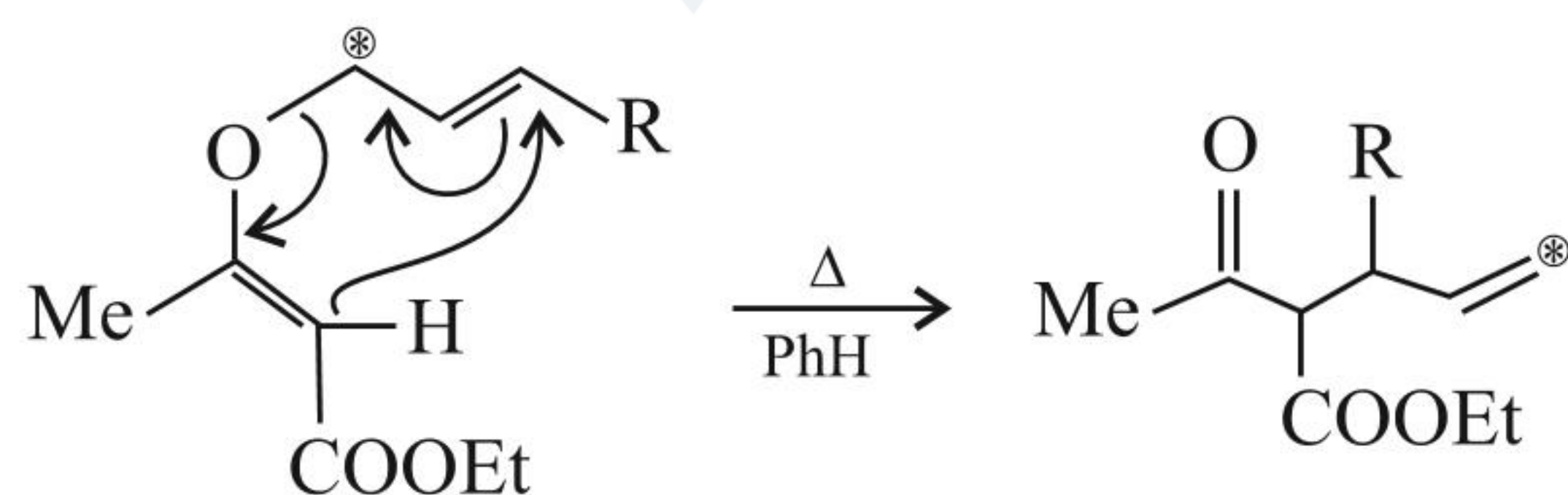
Example:

- v. The rearrangement is not restricted to aromatic ring systems only. Allyl ethers of enols, e.g., allyl vinyl ethers, also undergo Claisen rearrangement.

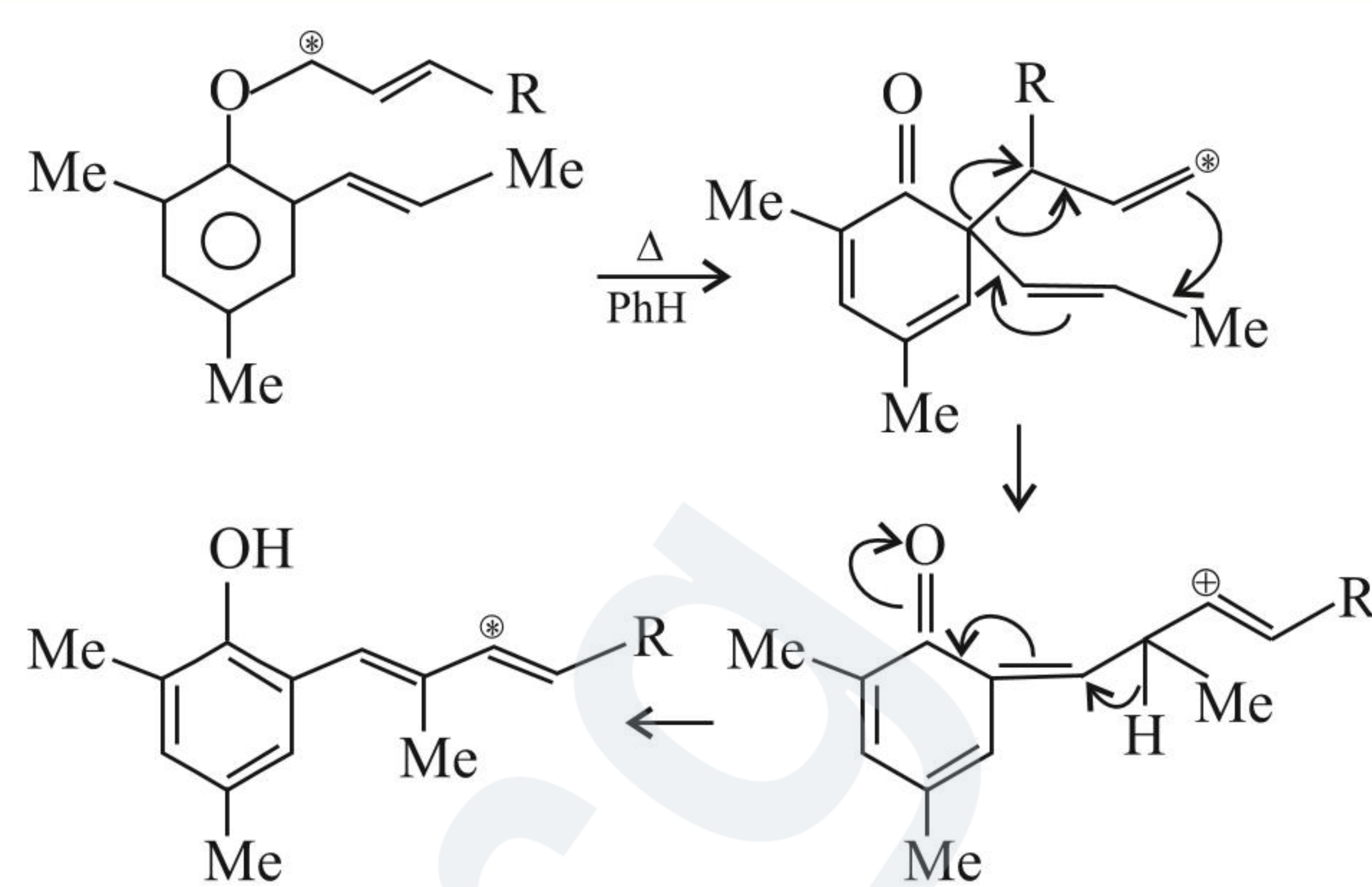


The product does not enolise (when R or R' = H) because ketones are more stable than enols.

- vi. The *o*-allyl acetoesters are also rearranged similarly.

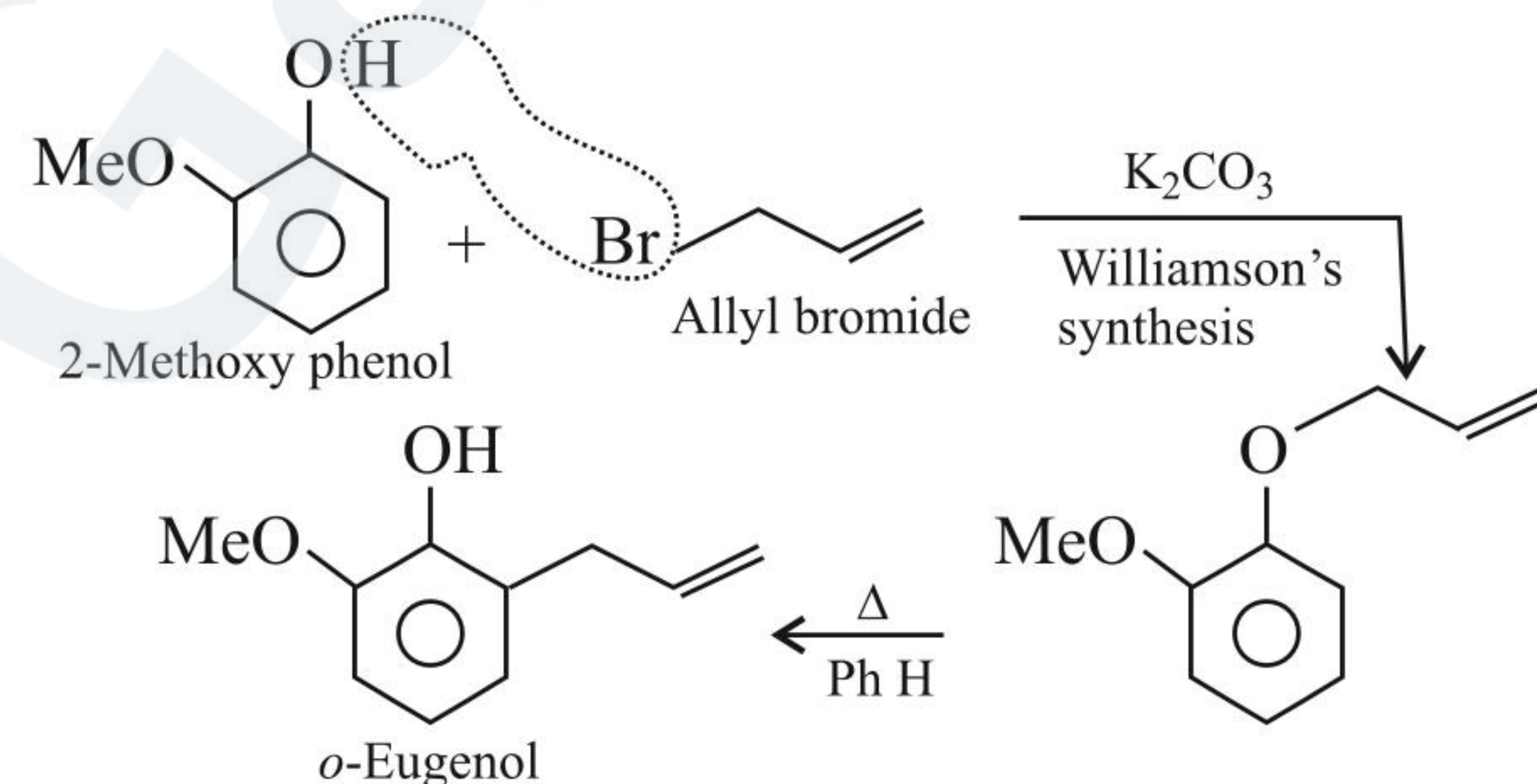


- vii. Out-of-ring rearrangement



There is no rearrangement of the allylic group in the final product due to double inversion.

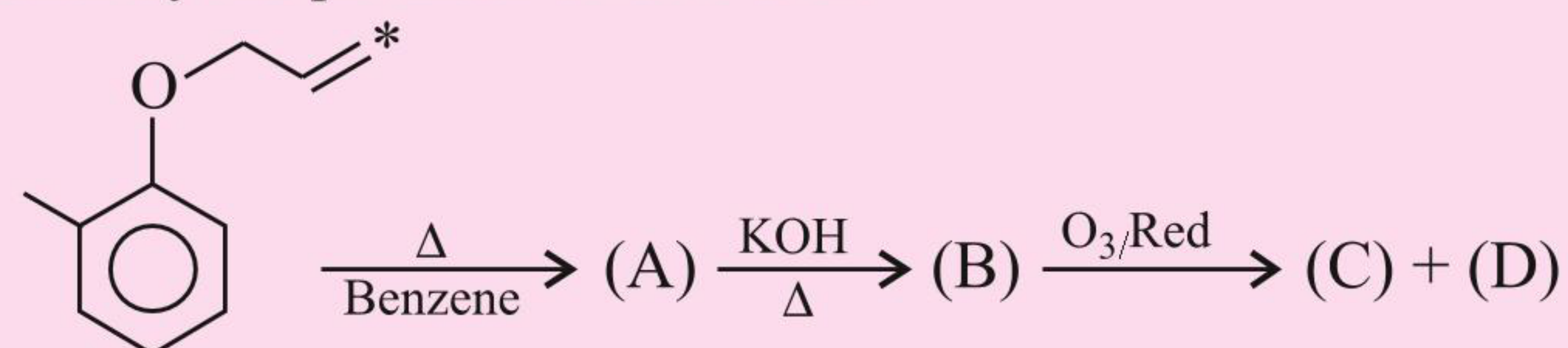
- viii. **Synthetic application:** Since aryl allyl ethers can be easily prepared, the rearrangement is employed to prepare various kinds of compounds, e.g.,



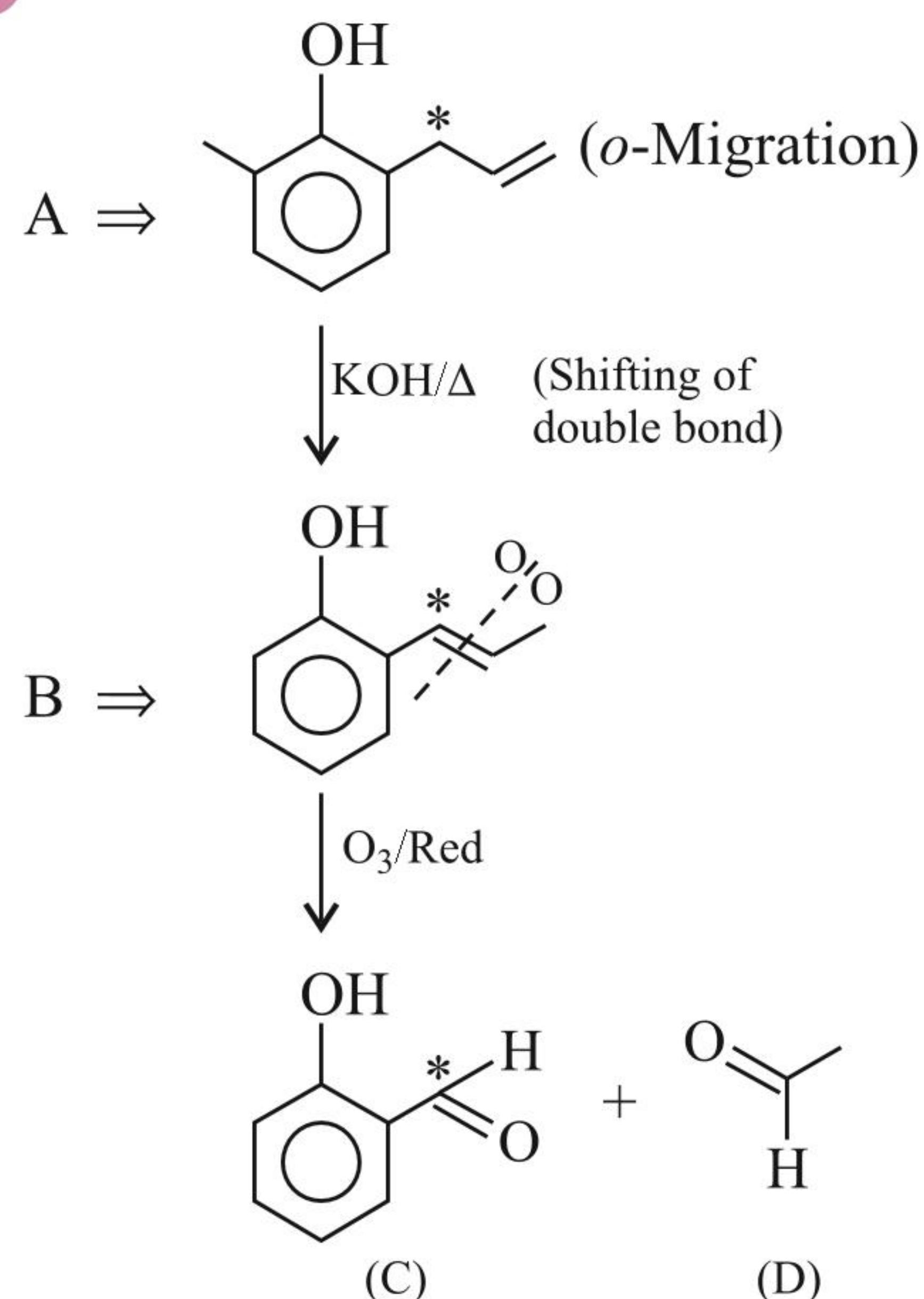
- ix. Various such derivatives may be prepared. Allyl aryl thioethers, e.g., Ar — S — CH₂ — CH = CH₂, do not ordinarily give *ortho* allyl thiophenols.

ILLUSTRATION 4.24

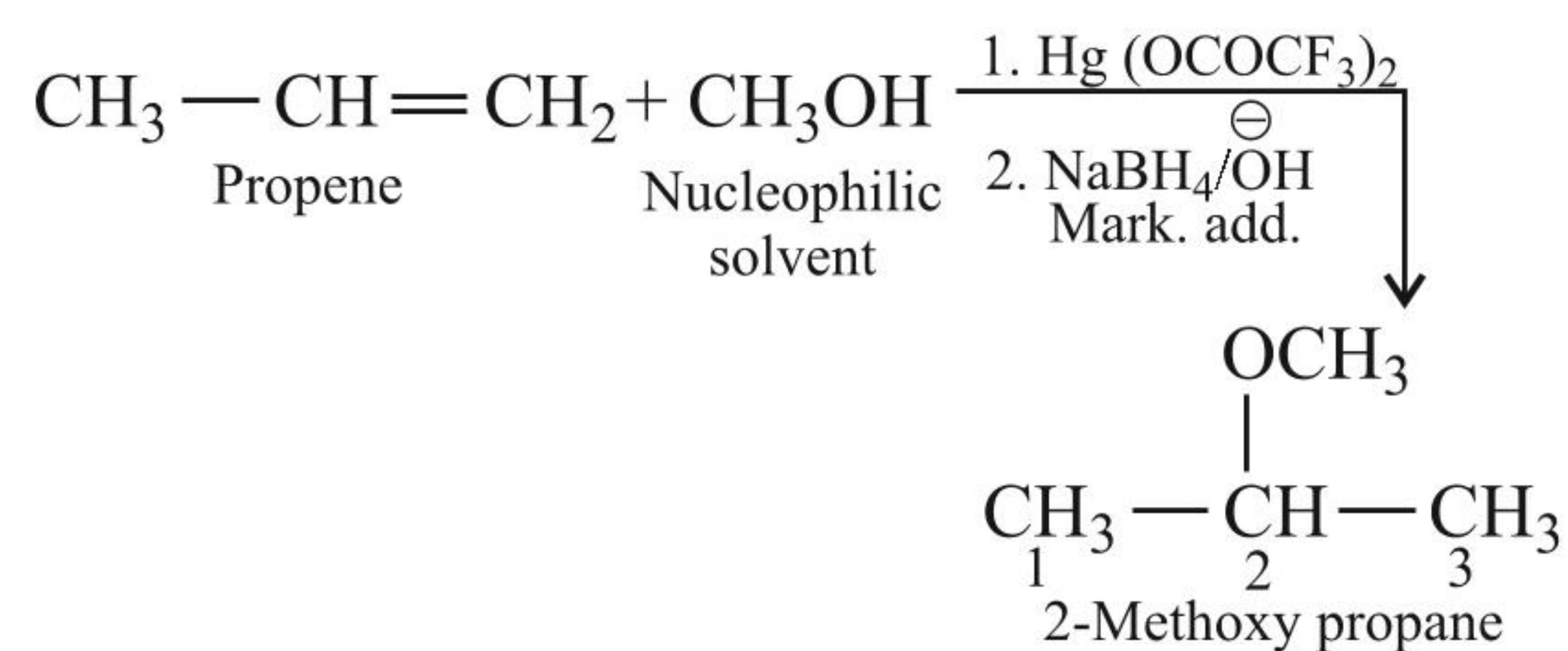
Identify the products from A to D.



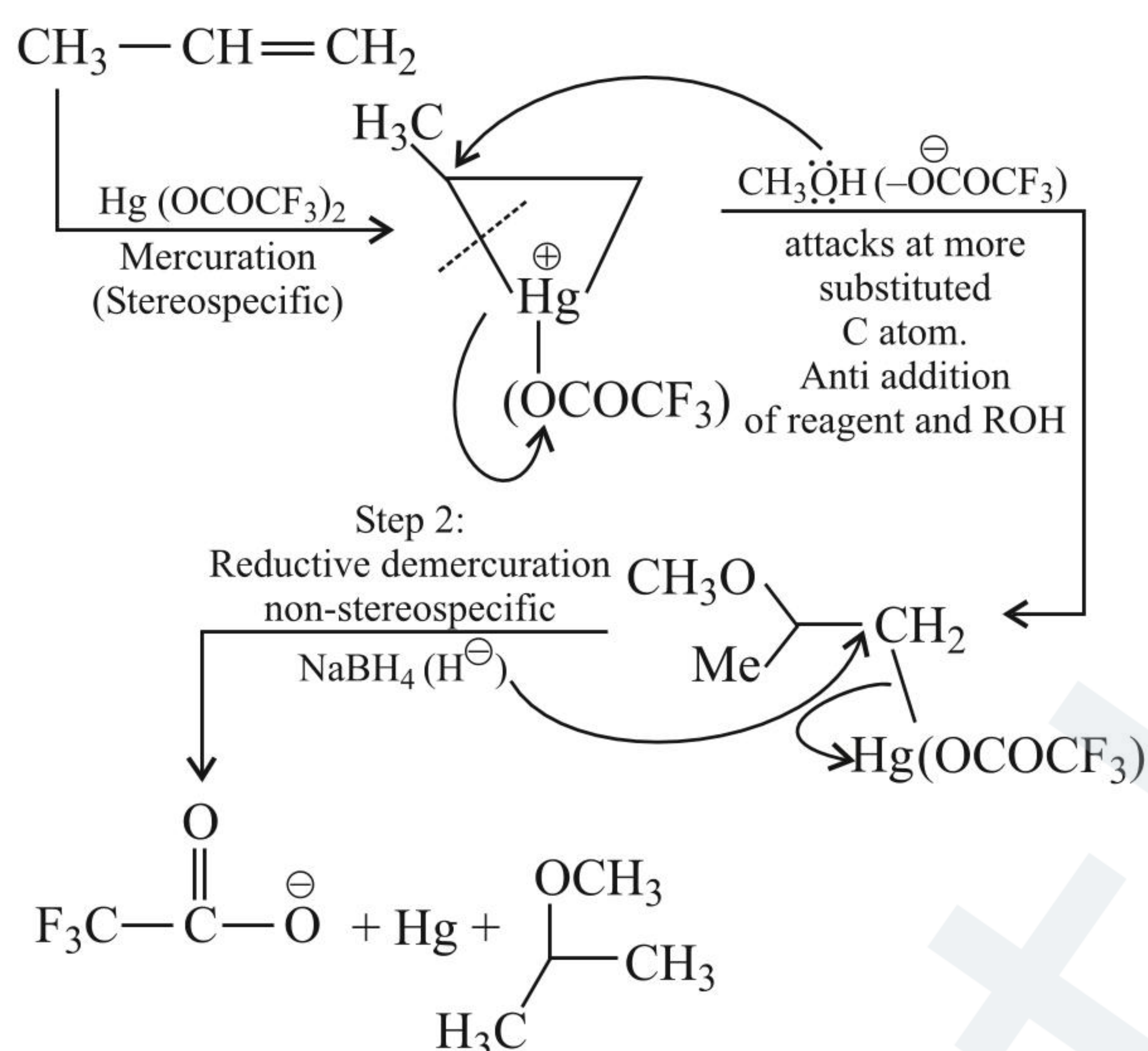
Sol.



4.35 ALKOXY MERCURATION-DEMERCURATION (A TYPE OF SOLVOMERCURATION-DEMERCURATION)



Mechanism:



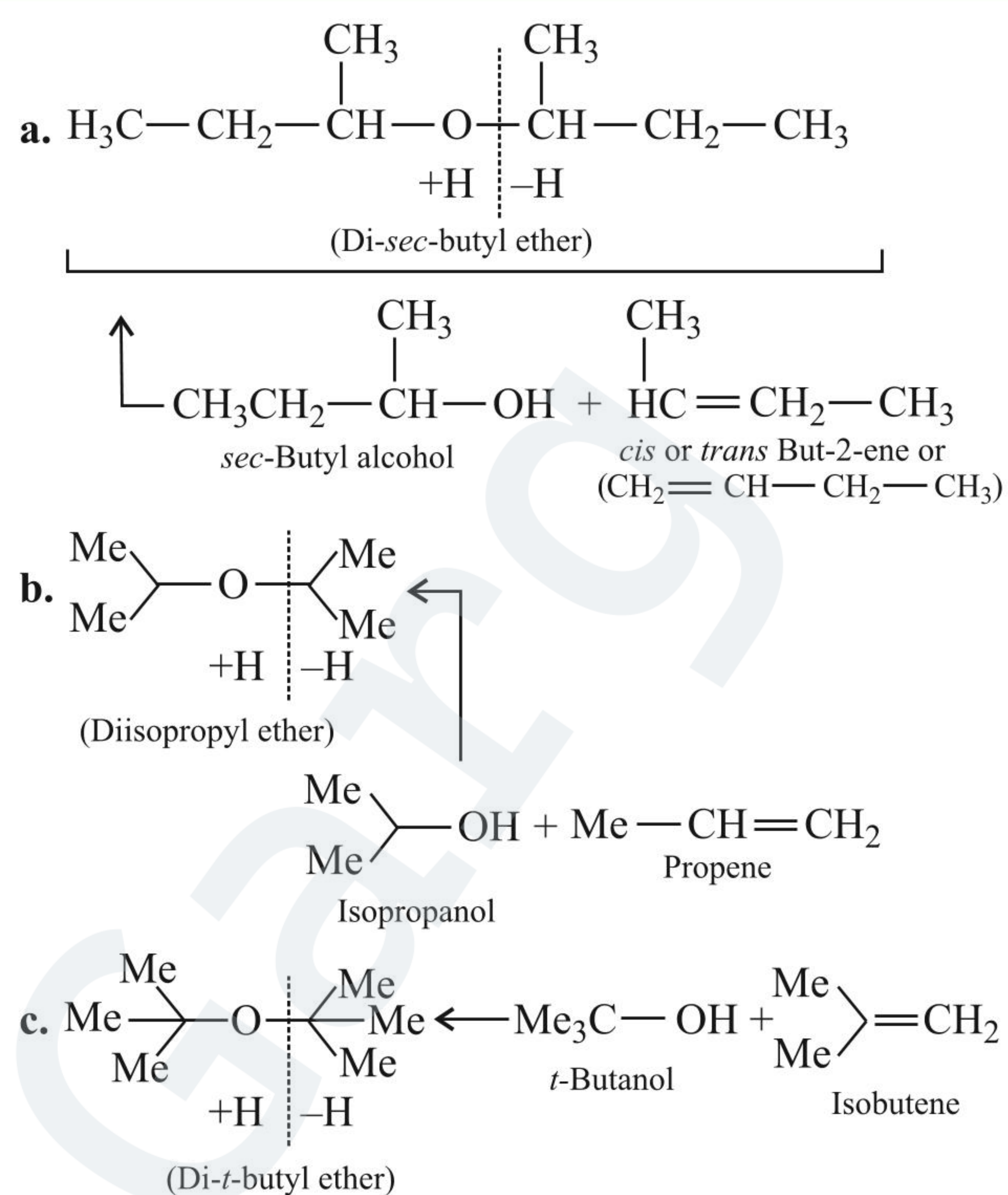
- In the first step, intermediate mercurinium ion is formed. Since no carbocation is formed so no rearrangement occurs.
- There is anti-addition of reagent and ROH. The ROH attacks from the backside on the more substituted C atom of the ring since the C atom bears more δ^+ charge. Frontside attack is blocked by large (HgOCOCF_3) group.
- Addition of ROH is in accordance with Markovnikov orientation.
- First step, i.e., mercuration step is stereospecific and second step, i.e., reductive demercuration with NaBH_4 is non-stereospecific and total reaction is also non-stereospecific.

ILLUSTRATION 4.25

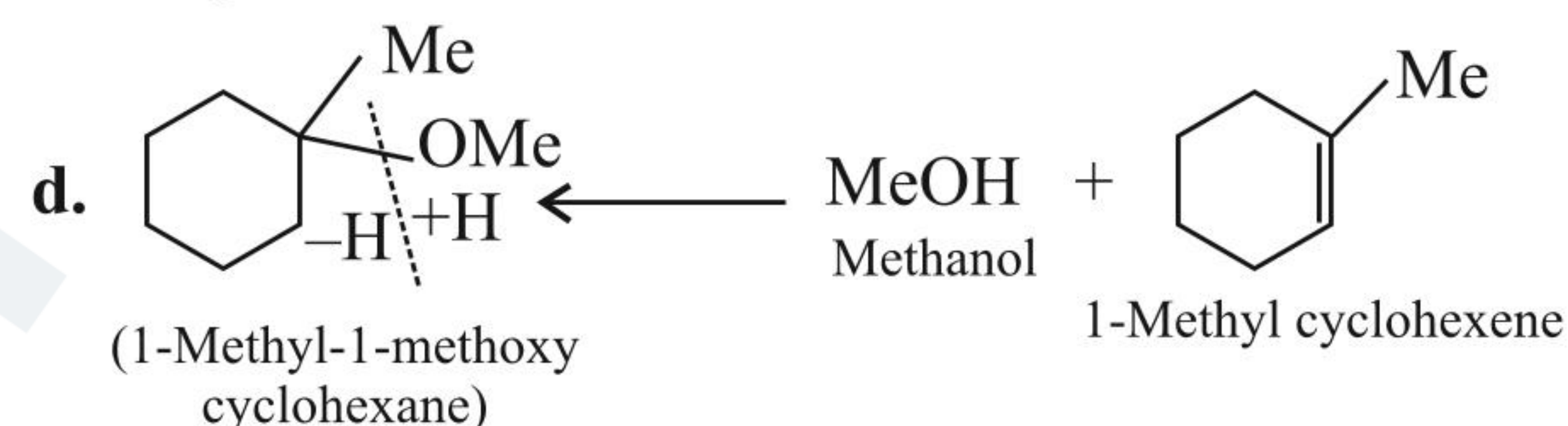
Give the alcohol and alkene required to prepare the following ethers by alkoxy mercuration-demercuration.

- Di-*sec*-butyl ether
- Di-isopropyl ether
- Di-*t*-butyl ether
- 1-Methyl-1-methoxy cyclohexane

Sol. Write the structures of ether, and then remove the alkoxy group to get the corresponding alkene and alcohol.

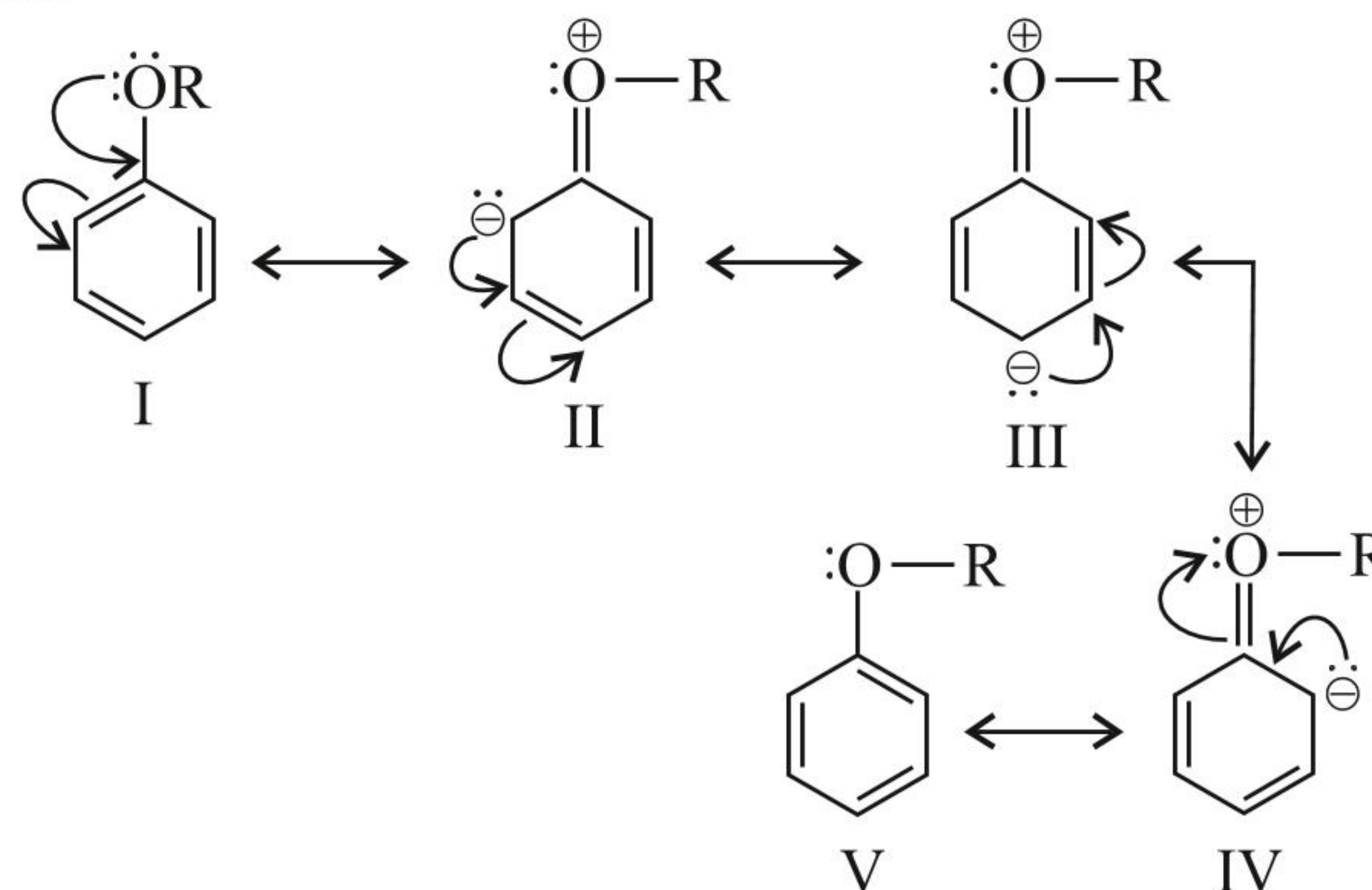


The yield of ethers with two 3° alkyl groups is poor because of high steric hindrance.



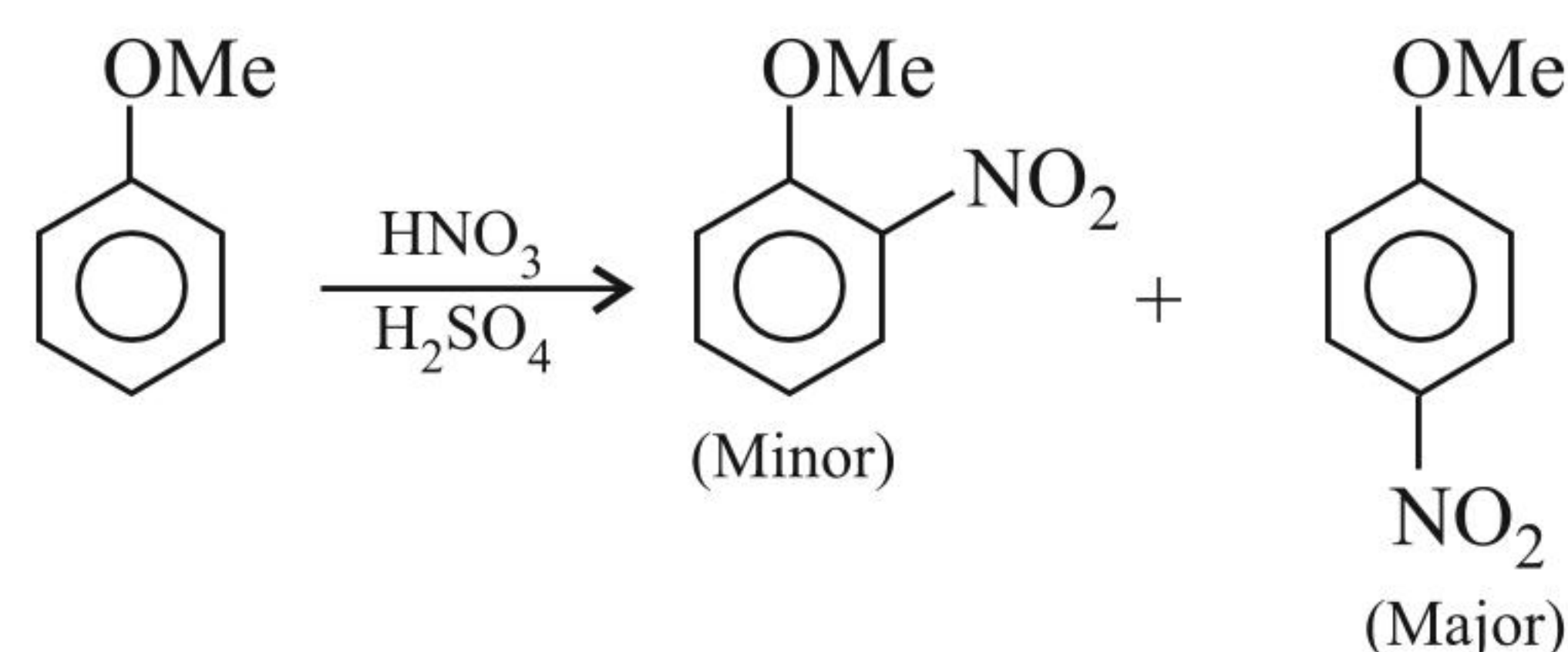
4.36 SE (SUBSTITUTION BY ELECTROPHILE) REACTIONS

The alkoxy group ($-\text{OR}$) is *o*- and *p*-directing and activates the benzene ring towards SE reaction in the same way as in phenol.



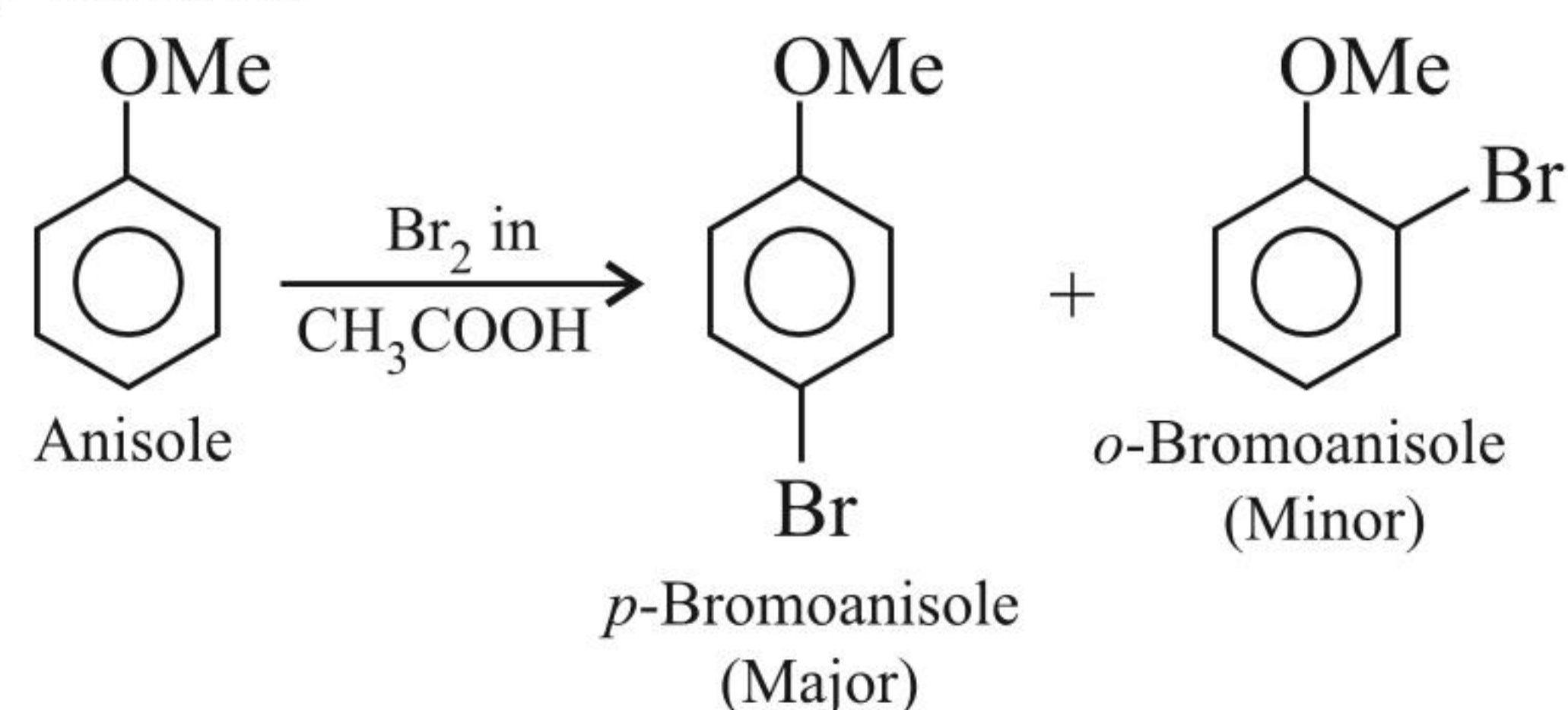
4.36.1 NITRATION

Anisole reacts with (conc. HNO_3 + Conc. H_2SO_4) to give *o*- and *p*-nitro anisole.



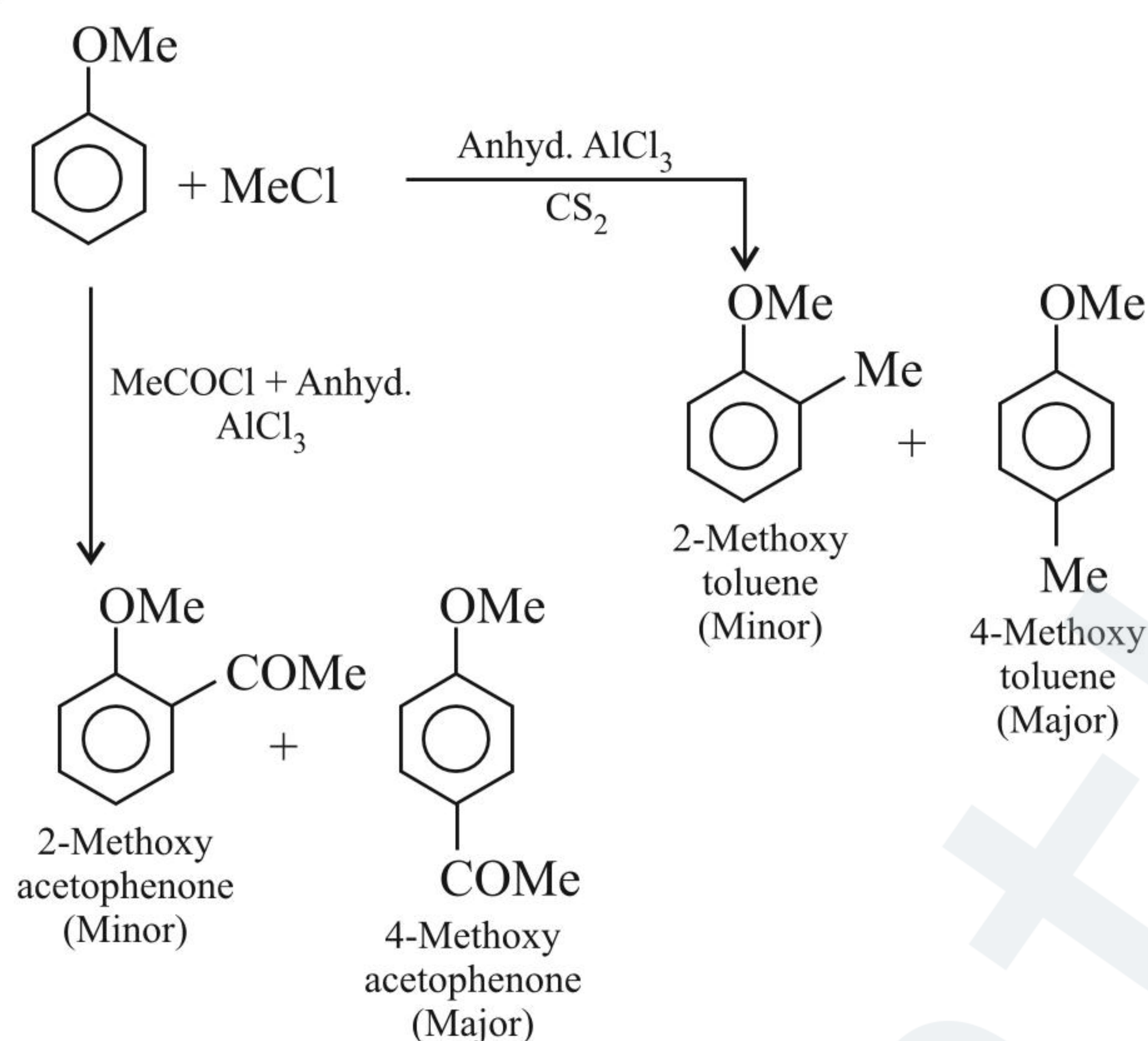
4.36.2 HALOGENATION

Due to the activation of benzene ring by methoxy group, anisole undergoes bromination with Br_2 in acetic acid even in the absence of FeBr_3 as catalyst and forms *o*- and *p*-bromoanisole with 90% yield of *p*-isomer.



4.36.3 FRIEDEL-CRAFTS REACTION

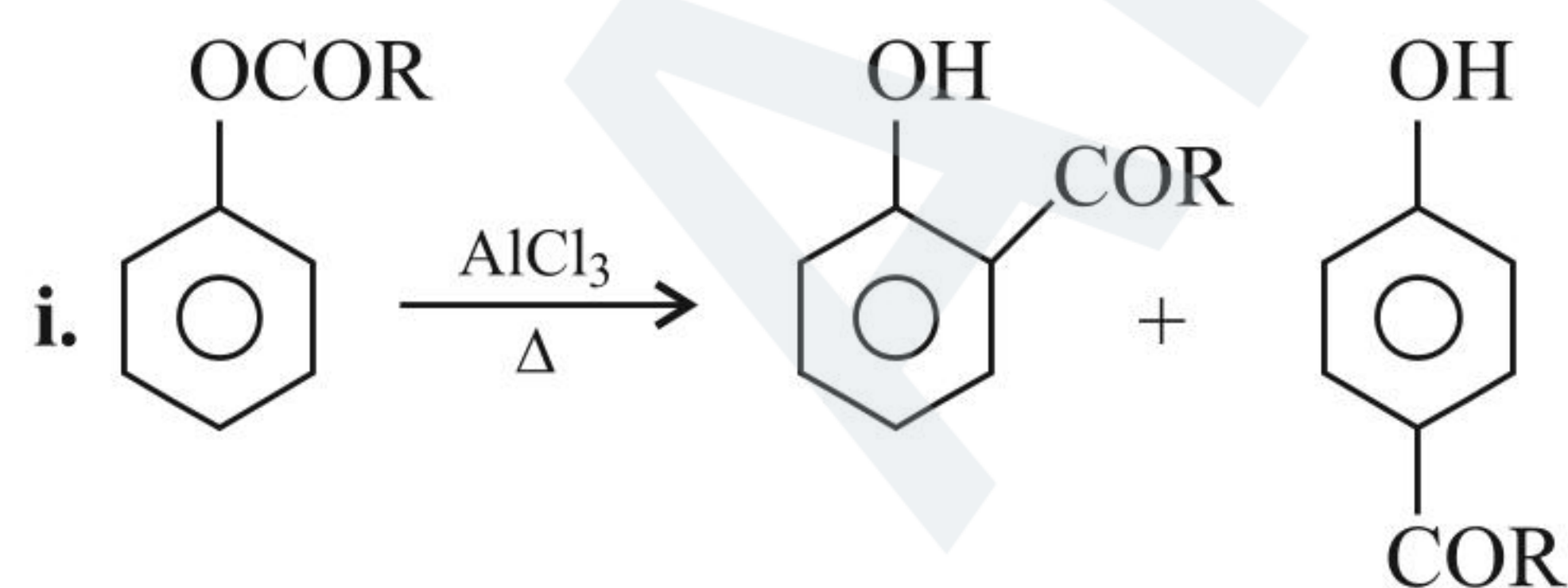
Anisole undergoes F.C. alkylation and acylation reaction in the presence of anhydrous AlCl_3 (Lewis acid) as catalyst to give *o*- and *p*-isomers.



4.37 FRIES REARRANGEMENT REACTION

Phenolic esters with AlCl_3 give *o*- and *p*-acyl phenol. At low temperature ($<100^\circ\text{C}$) *para*-form predominates and at high temperature ($>100^\circ\text{C}$) *ortho*-form predominates (\bar{e} - withdrawing group in the substrate retards the reaction as in Friedel-Crafts reaction).

Example: This reaction proceeds *via* concerted mechanism (pericyclic like Claisen rearrangement).



(Separated by steam distillation, *ortho* form has a lower boiling point due to H-bonding.)

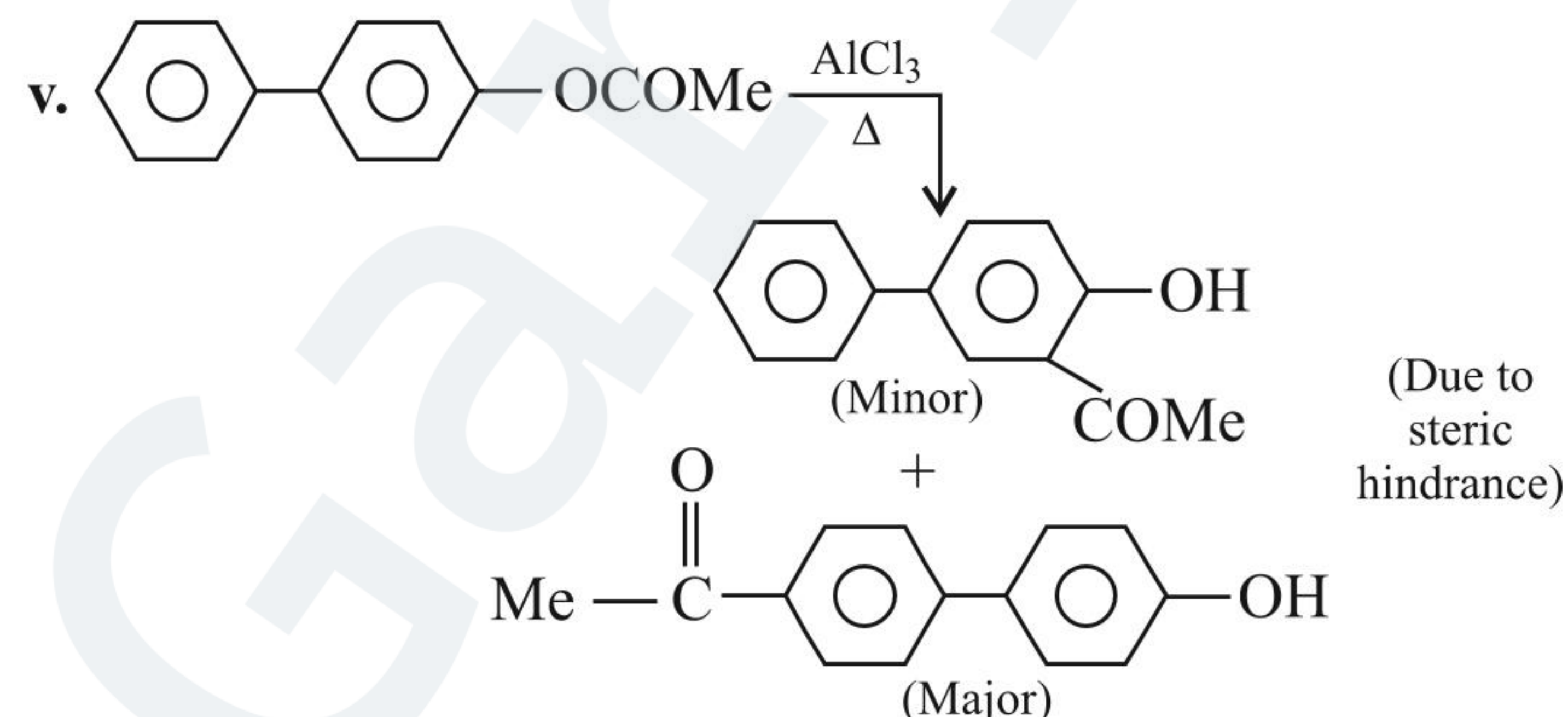
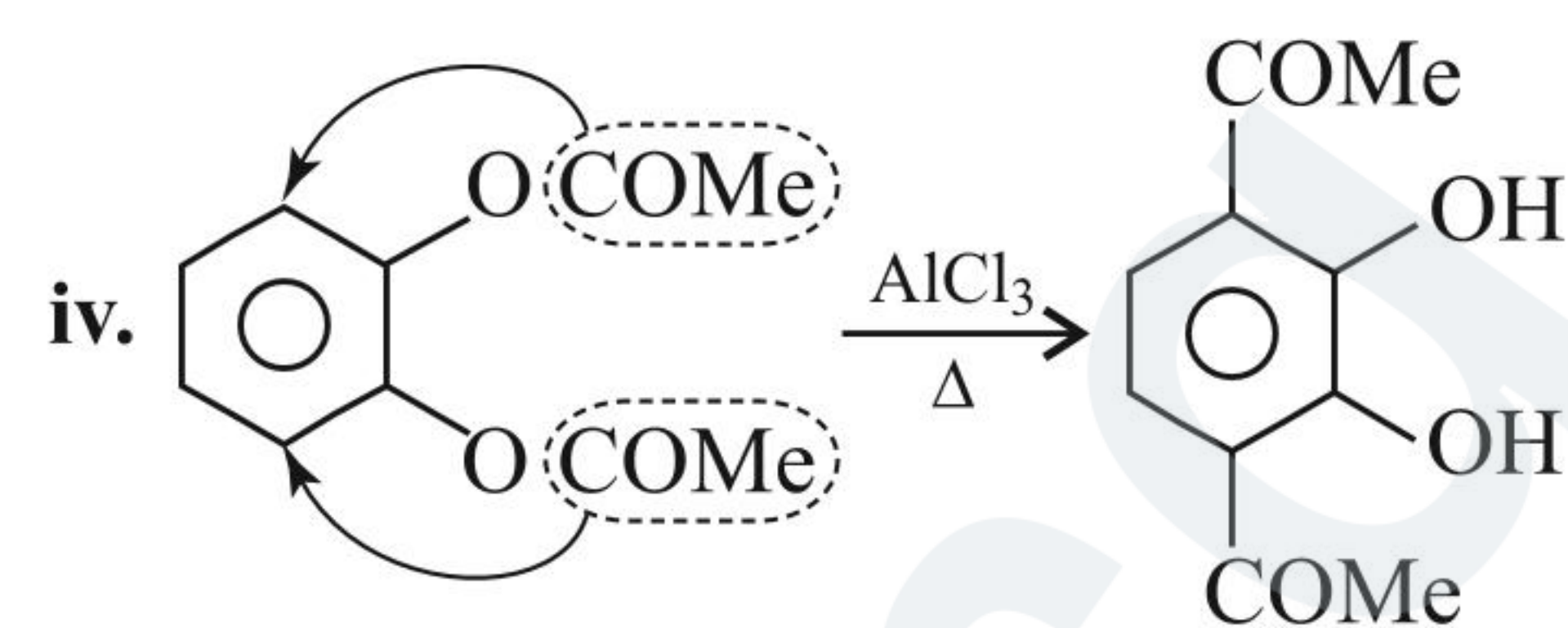
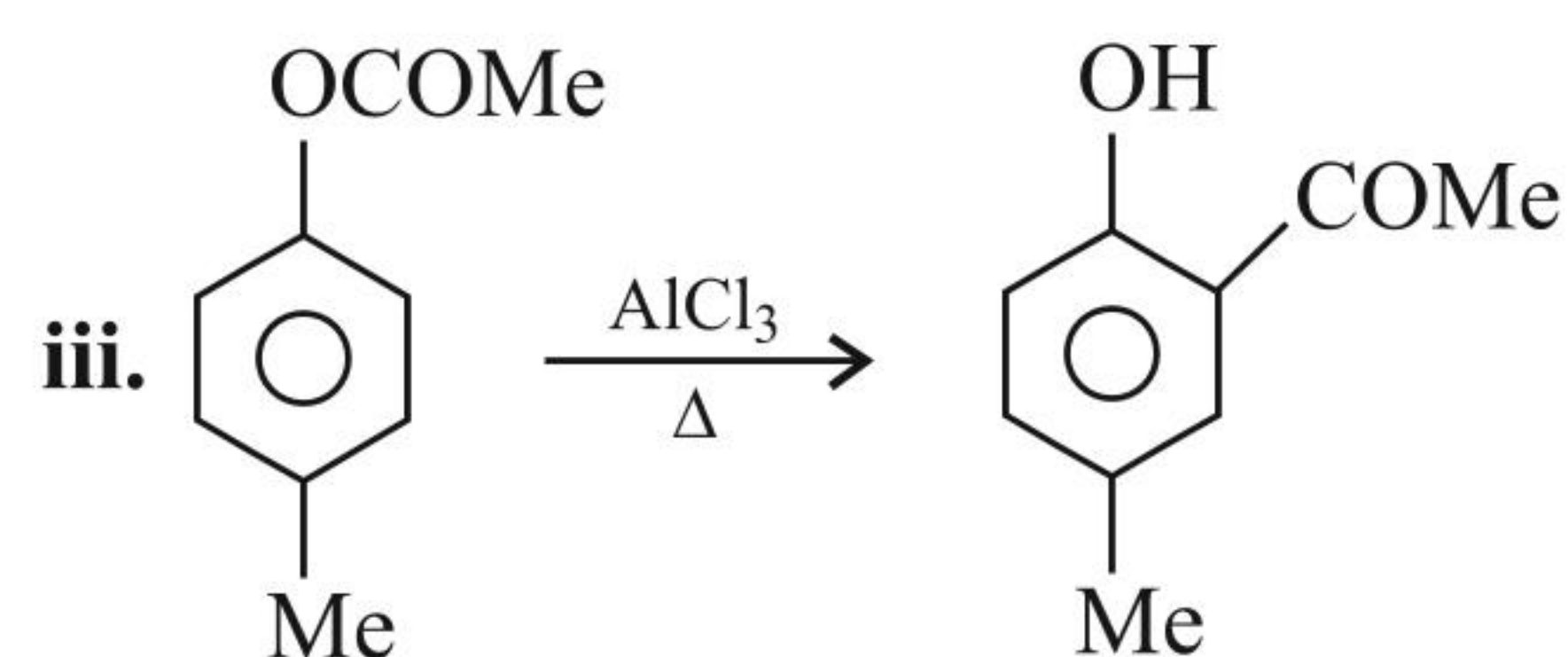
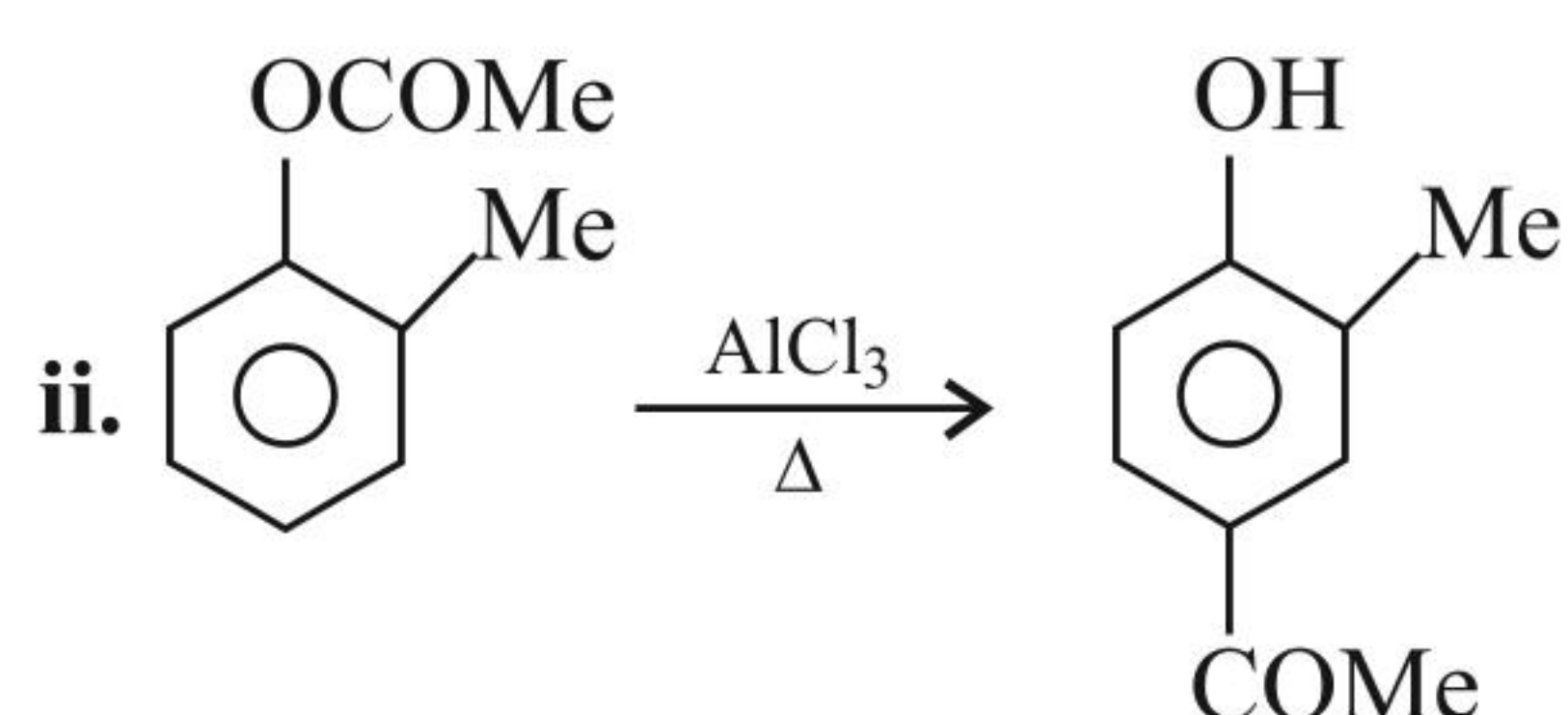
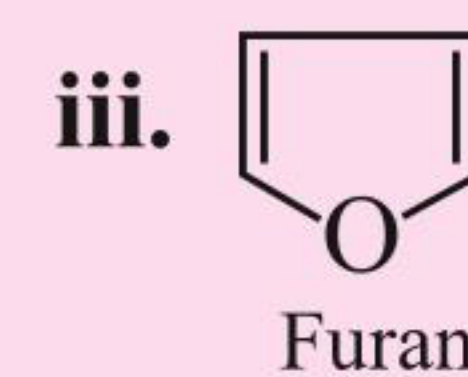
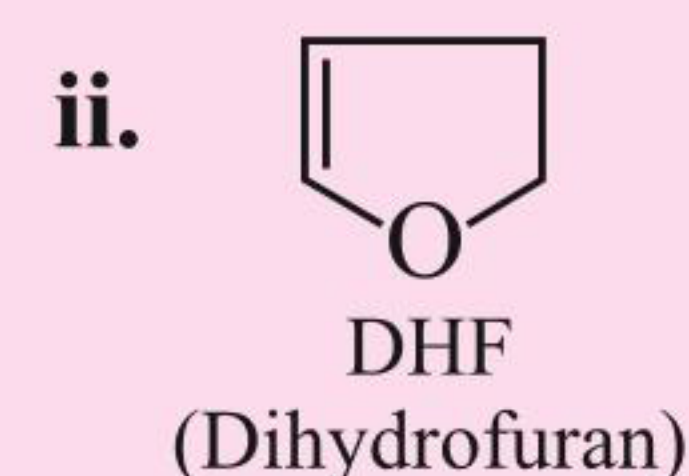
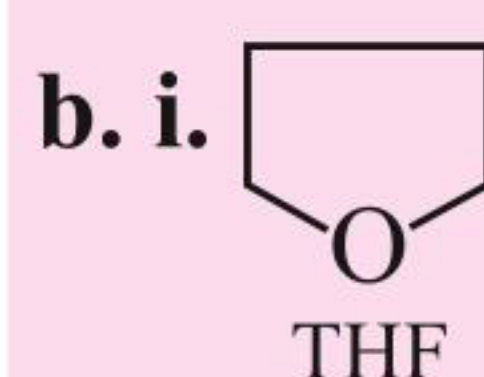
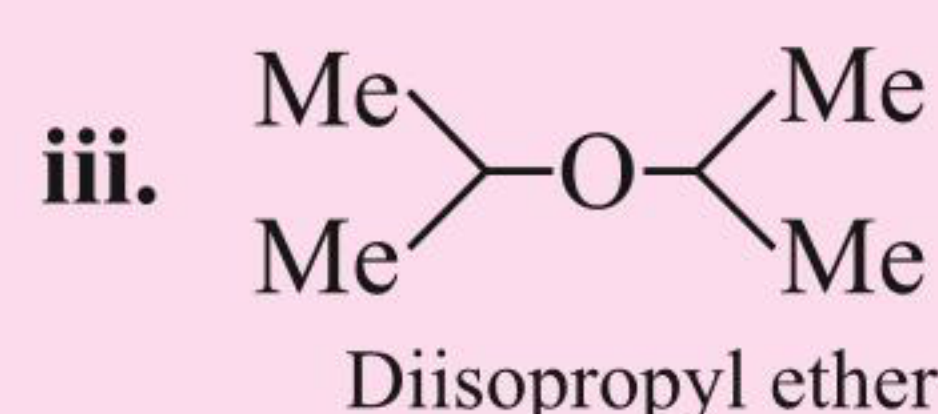
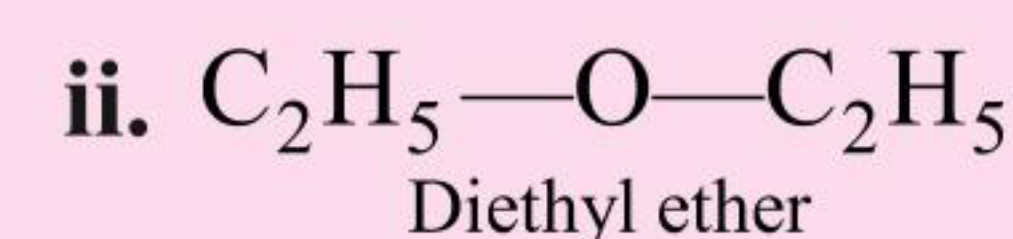
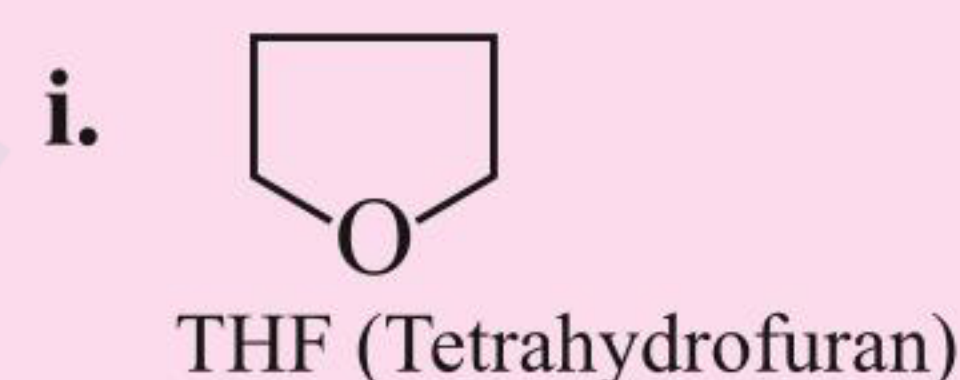
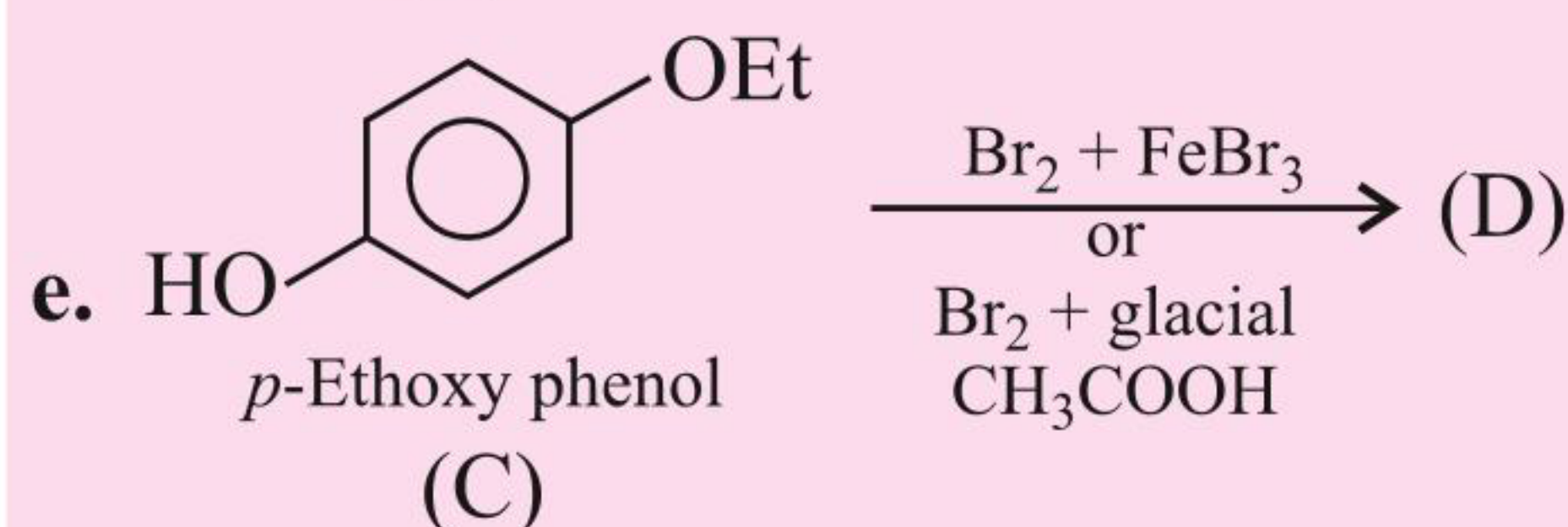
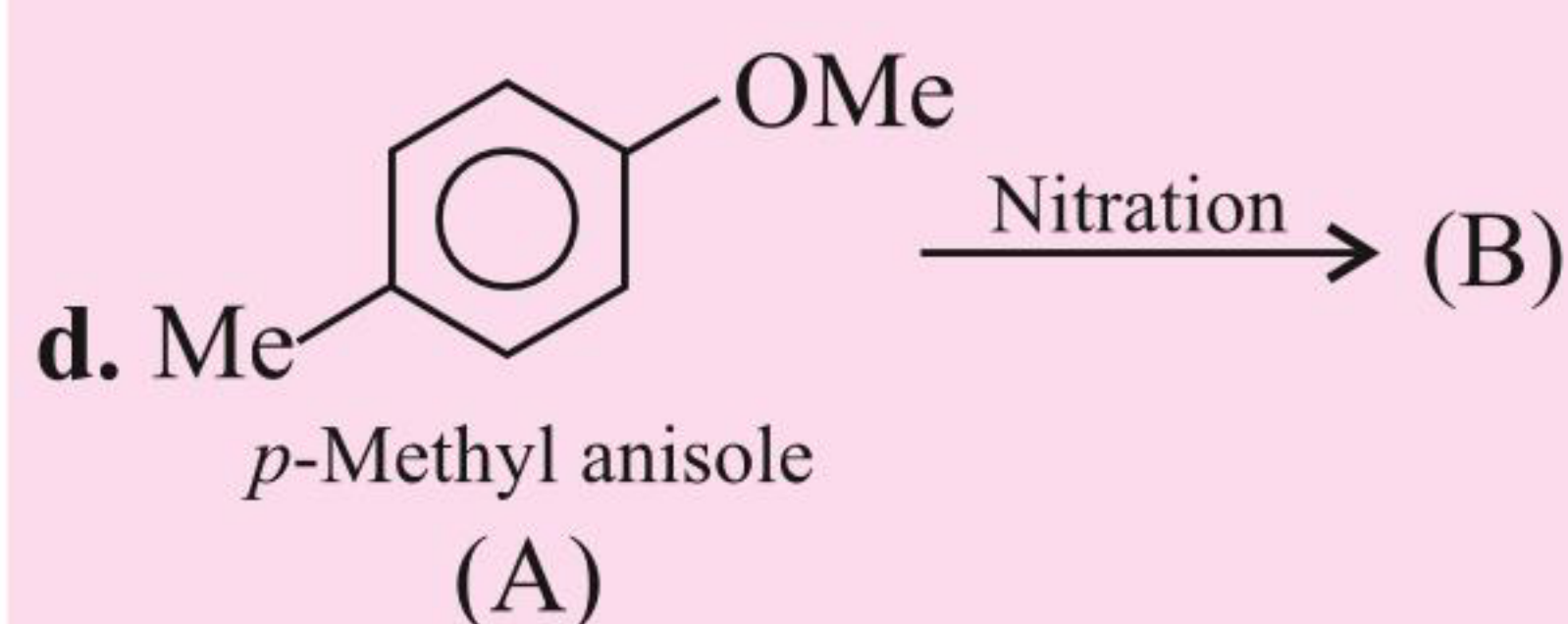
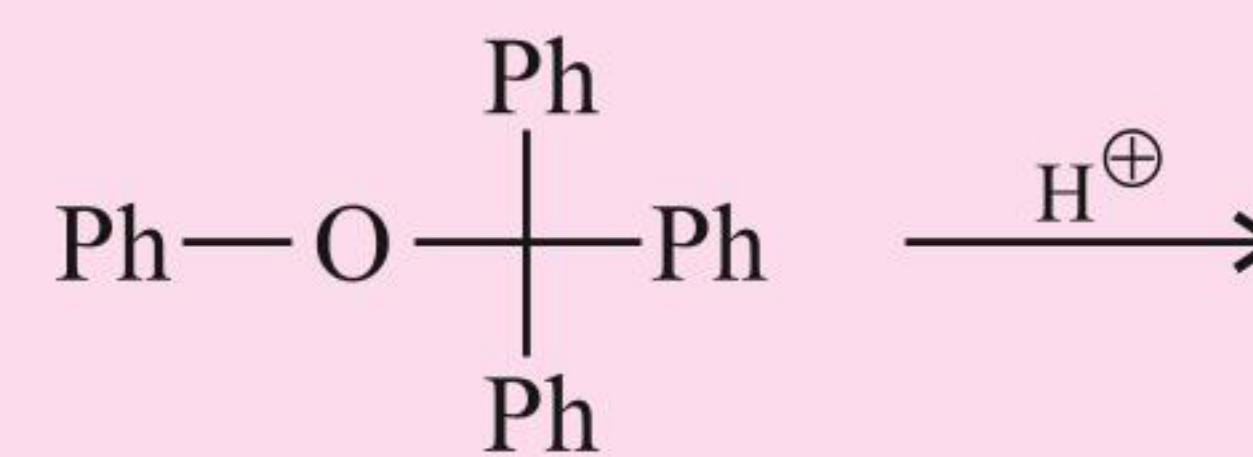


ILLUSTRATION 4.26

a. Give the decreasing order of Lewis basicities of the following:



c. Complete the following reaction:



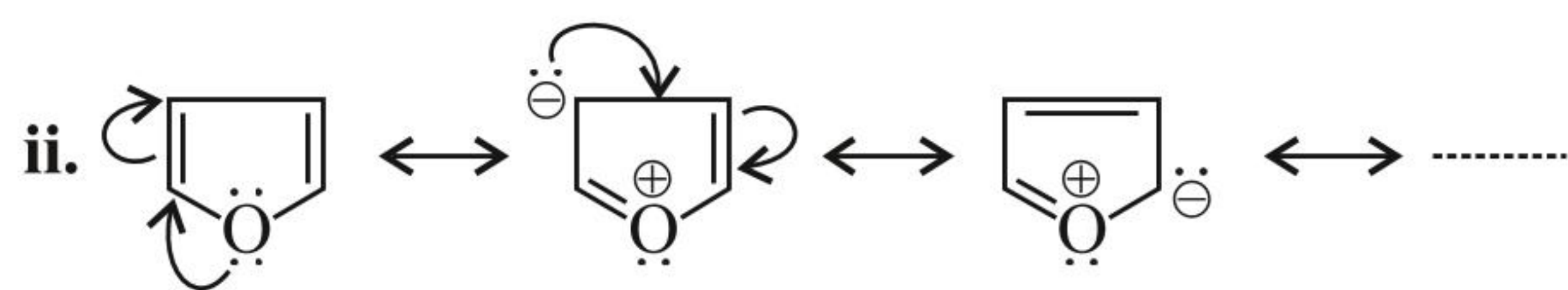
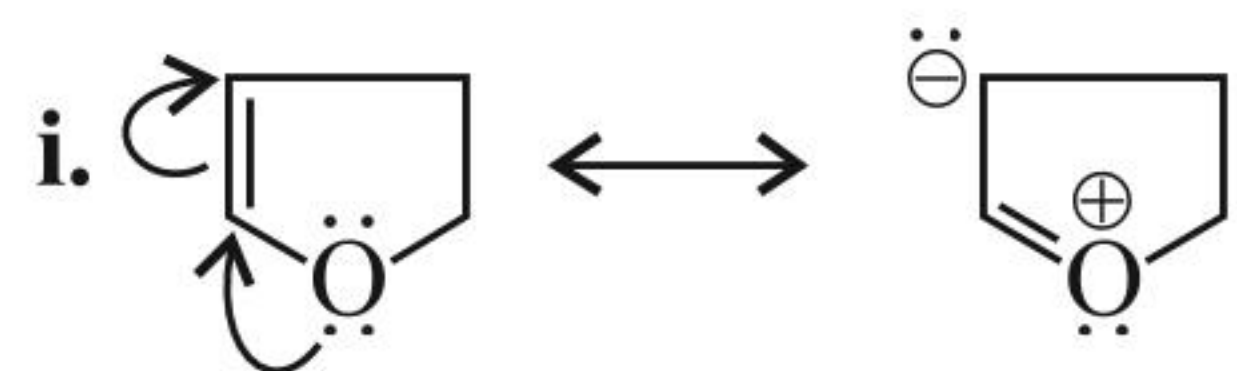
Sol.

a. Greater the steric hindrance in the ether molecule encountered in the formation of the coordinate bond, weaker is the Lewis basicity. In (i), R groups (the side of the ring) are 'tied back'

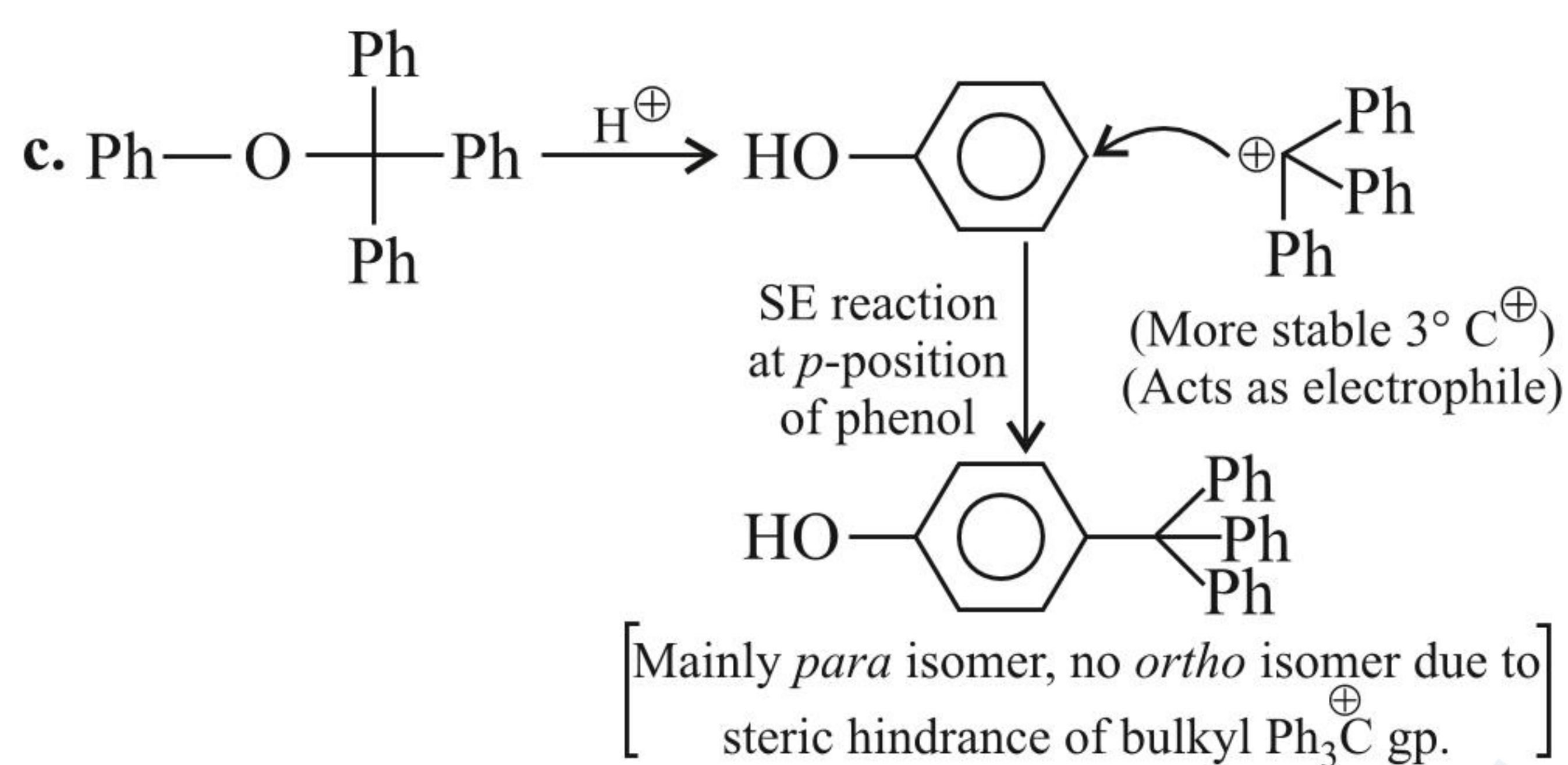
leaving a very exposed O atom free to serve as basic site. In other words, more compact the molecule (due to ring), more easily O atom can donate its LP \bar{e} 's to the Lewis acid, and therefore, stronger the Lewis base.

The decreasing order of Lewis basicities: (i) > (ii) > (iii).

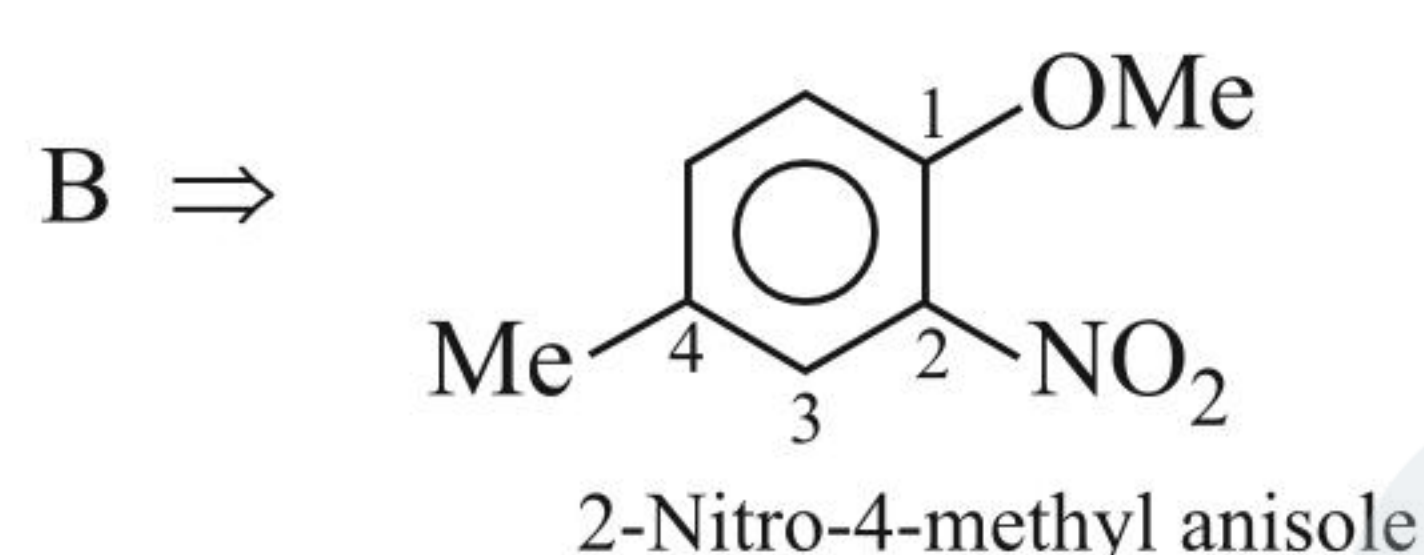
- b. In (ii) and (iii), the LP \bar{e} 's density is decreased due to resonance. But the decrease in LP \bar{e} 's density is more pronounced in (iii) than in (ii), due to more resonating structures.



Decreasing order of Lewis basicities: (i) > (ii) > (iii).



- d. (—OMe) group is activating group and *o*- and *p*-directing; since *p*-position is blocked. So (—NO₂) group enters at *o*-position w.r.t. (—OMe) group.



- e. The (—OH) group is a somewhat stronger activator than (—OR) group, thus (—Br) enters at *ortho* position w.r.t. (—OH) group (since *p*-position is blocked). A minor amount of 3-bromo product is also obtained.

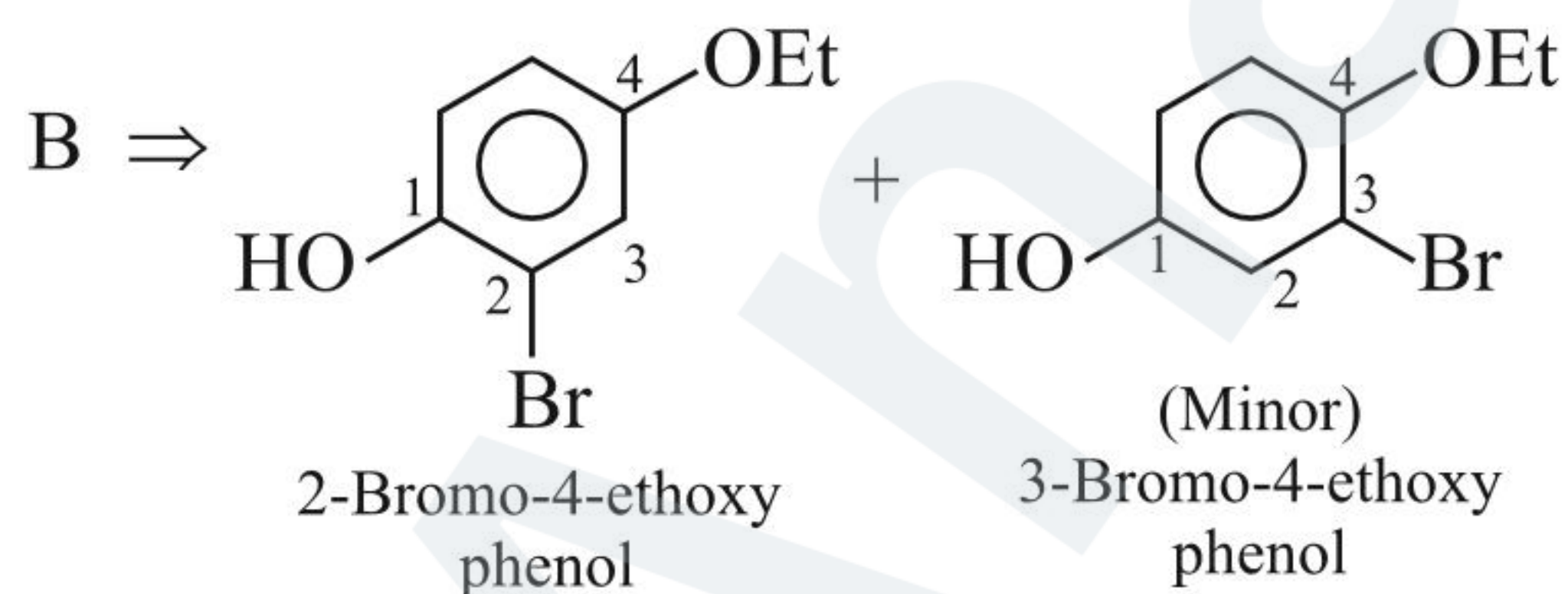
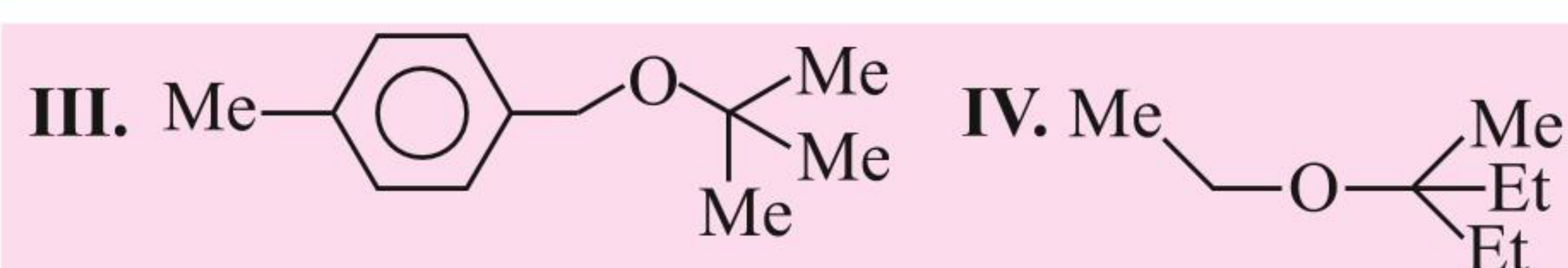
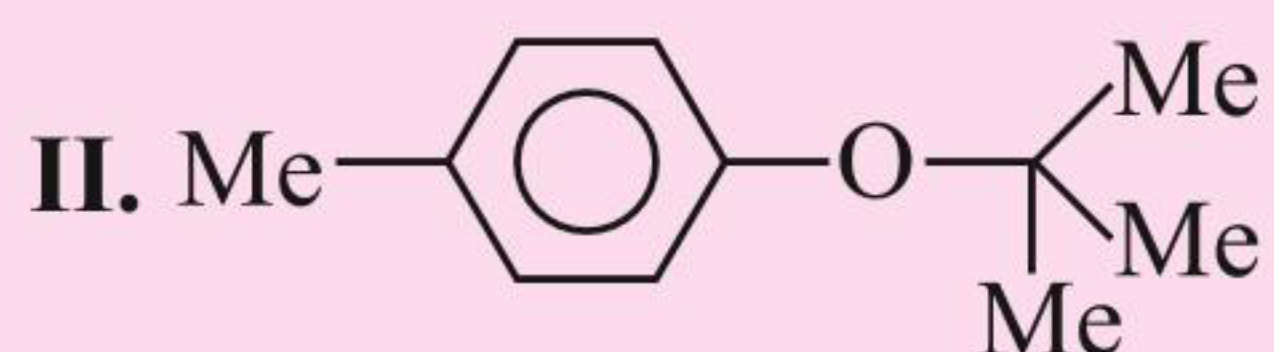


ILLUSTRATION 4.27

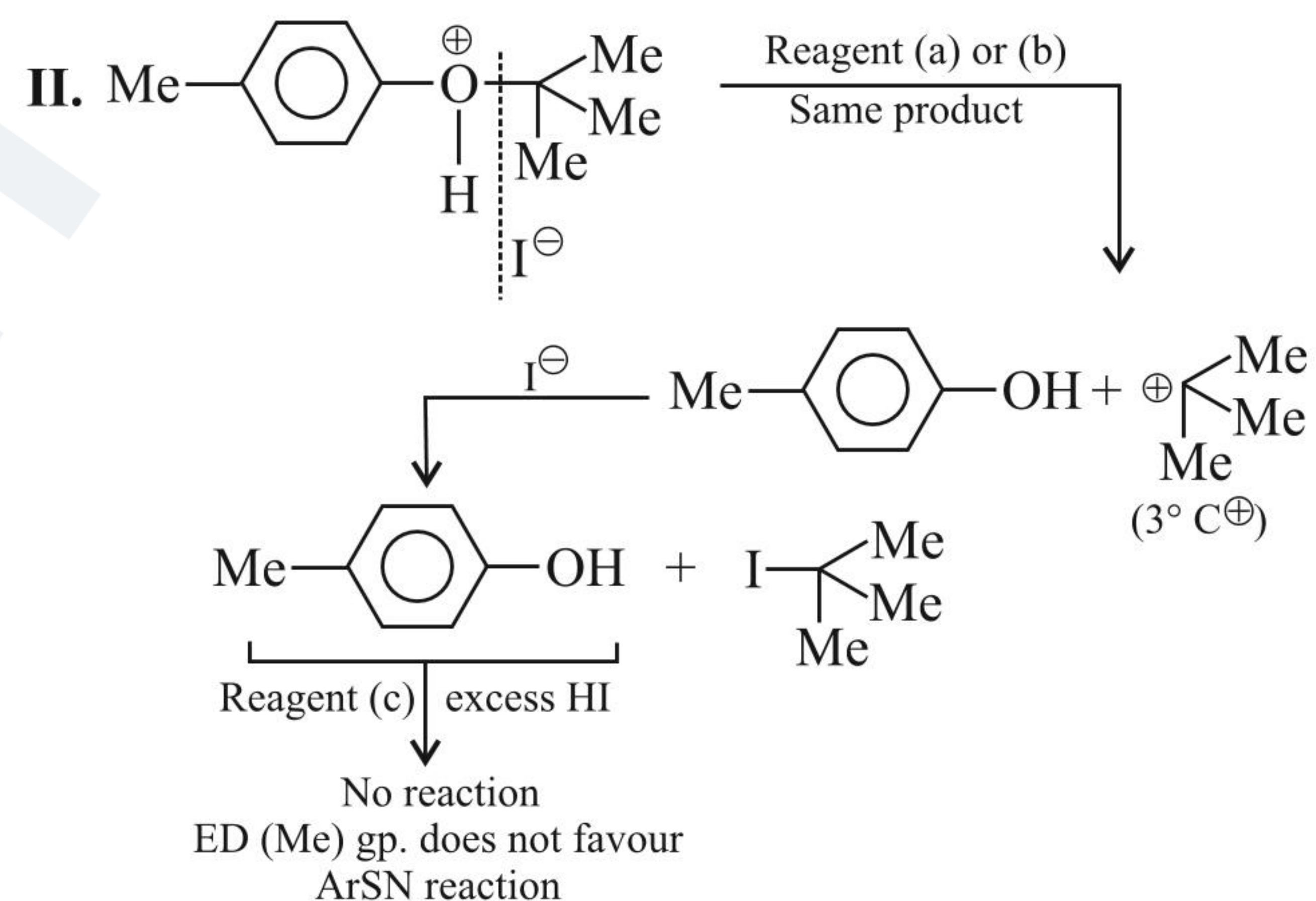
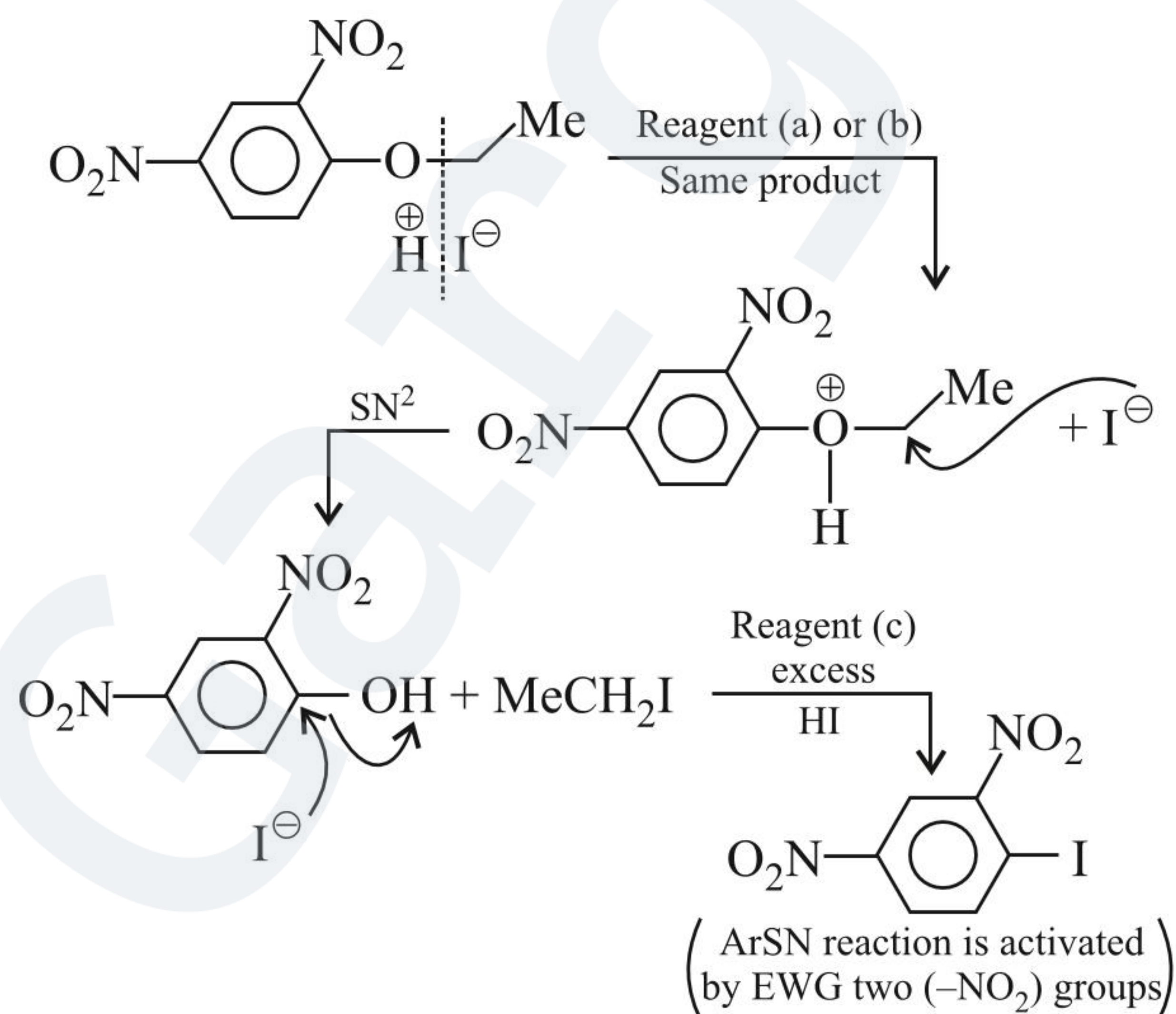
Give the products of the following ethers with:

- Aqueous HI
- Anhydrous HI + ether
- Excess of aq. HI

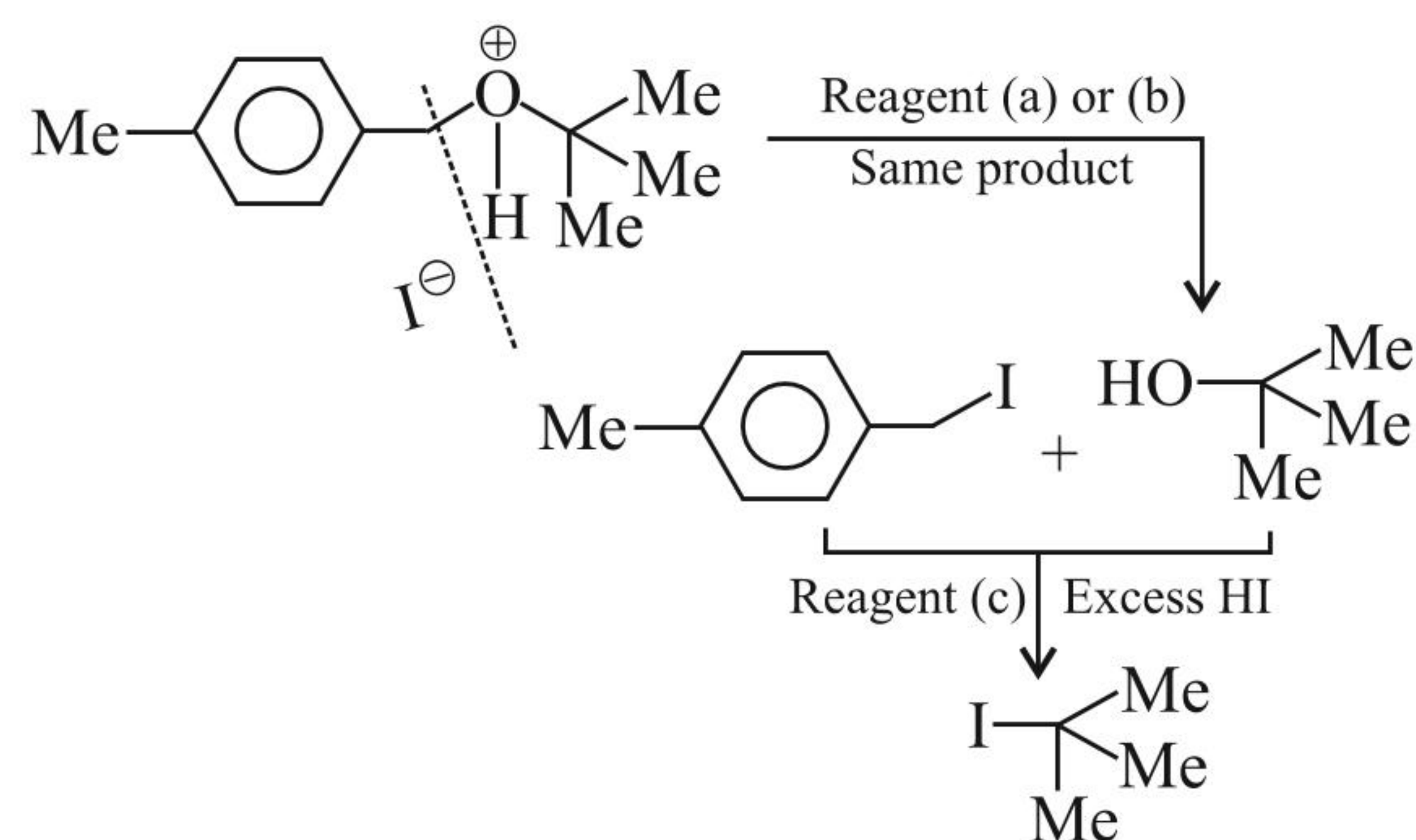


Sol.

- I. With reagent (a) and (b), products are same, since no 3° C⁺ is formed.



- III. In reagent (a), the high polarity of solvent (H₂O) favours S_N1 reaction, whereas in reagent (b), the low polarity of solvent (ether) favours S_N2 reaction. Since benzyl C⁺ is more stable (also stabilised by +I and hyperconjugative (H.C.) effect of (Me) group at *p*-position) than 3° C⁺, with benzyl C⁺ both S_N1 and S_N2 reactions are favoured. So the products from reagents (a) and (b) would be same.



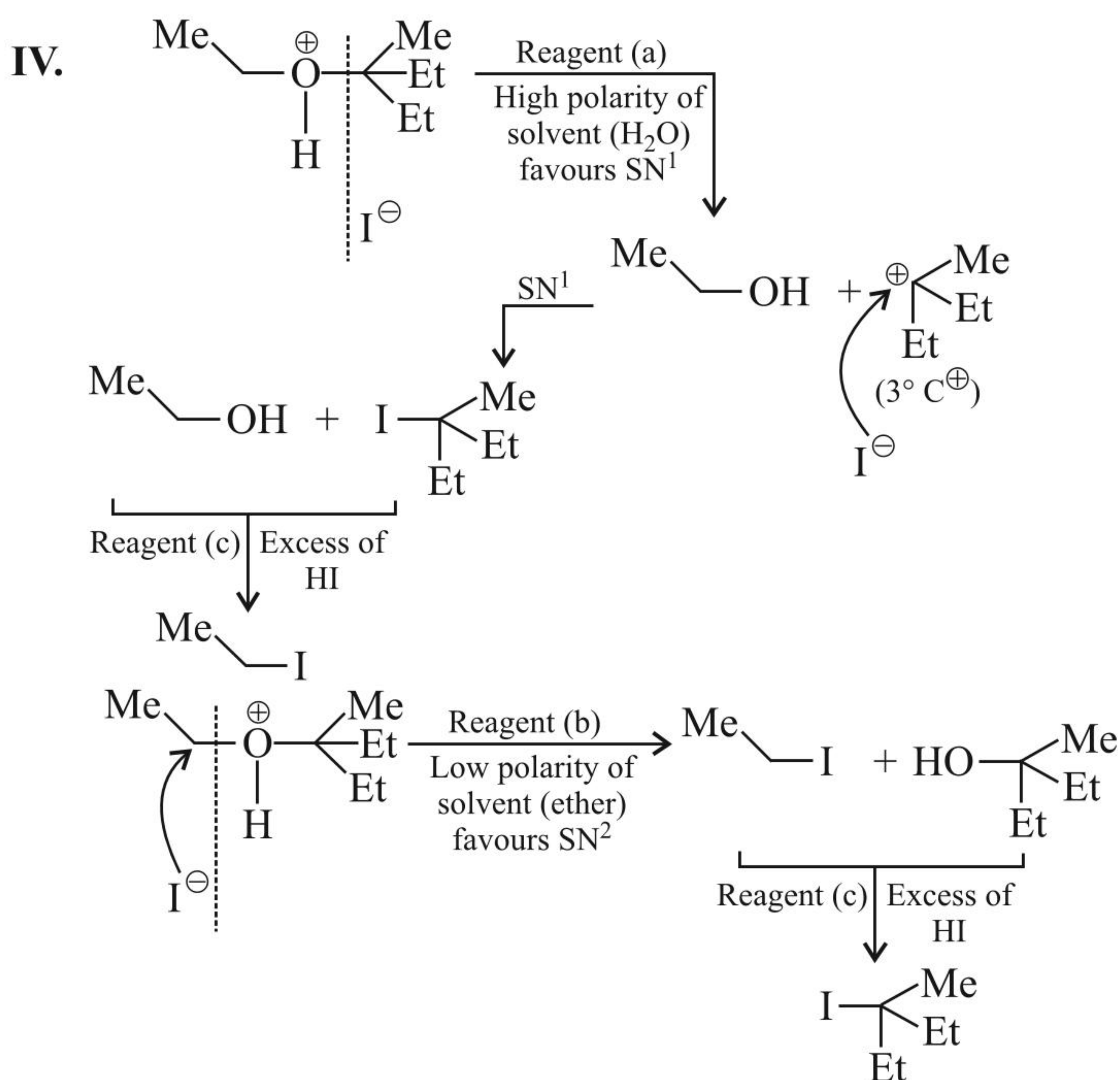
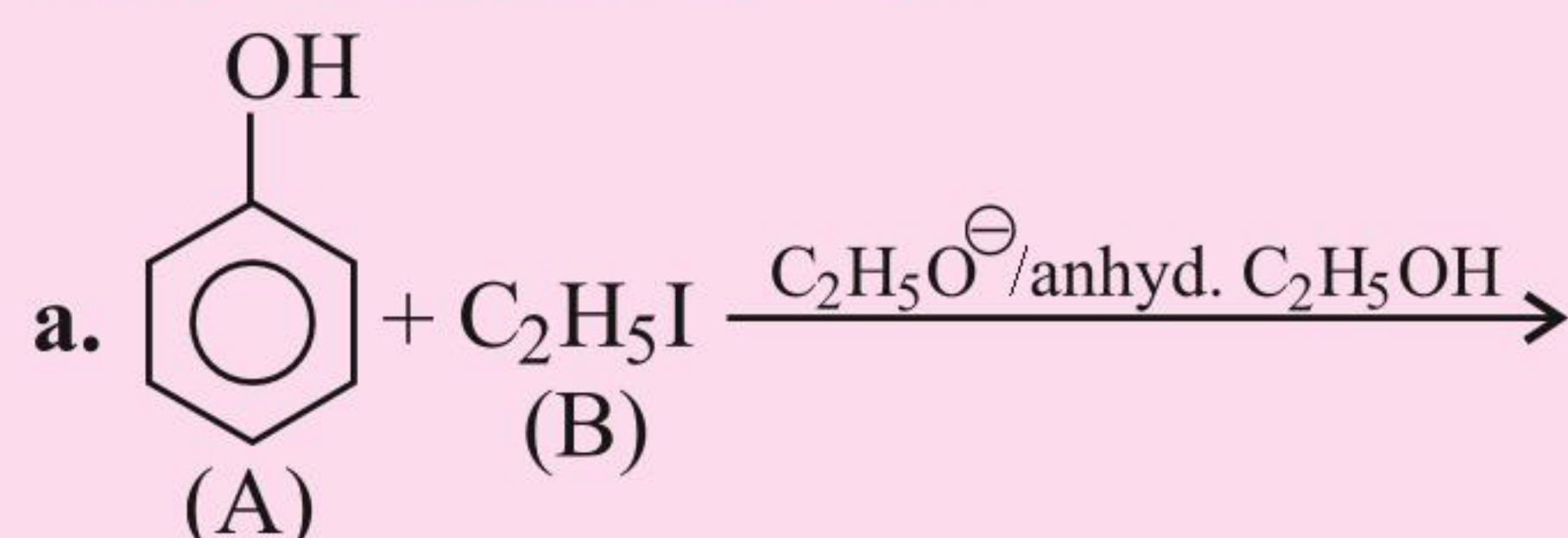


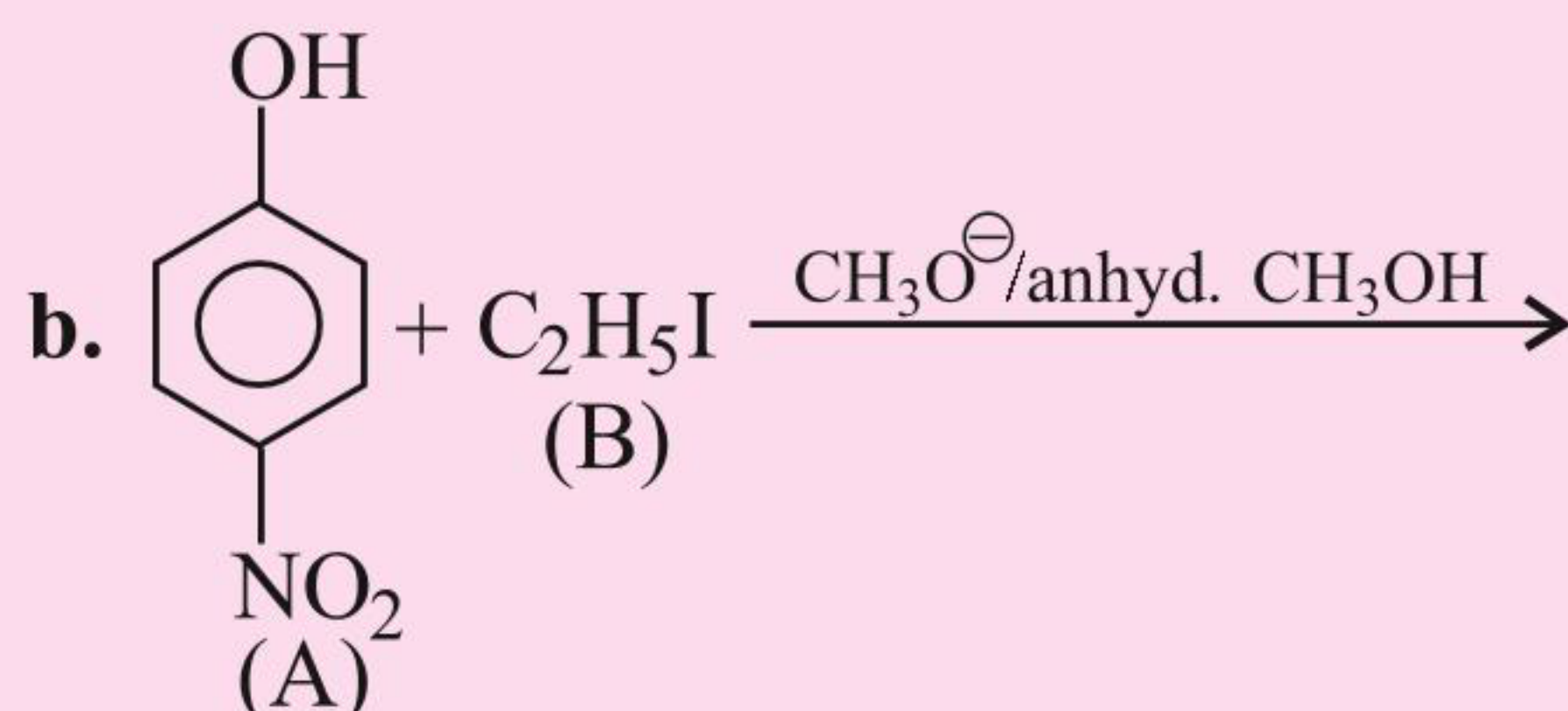
ILLUSTRATION 4.28

Select the correct answer:

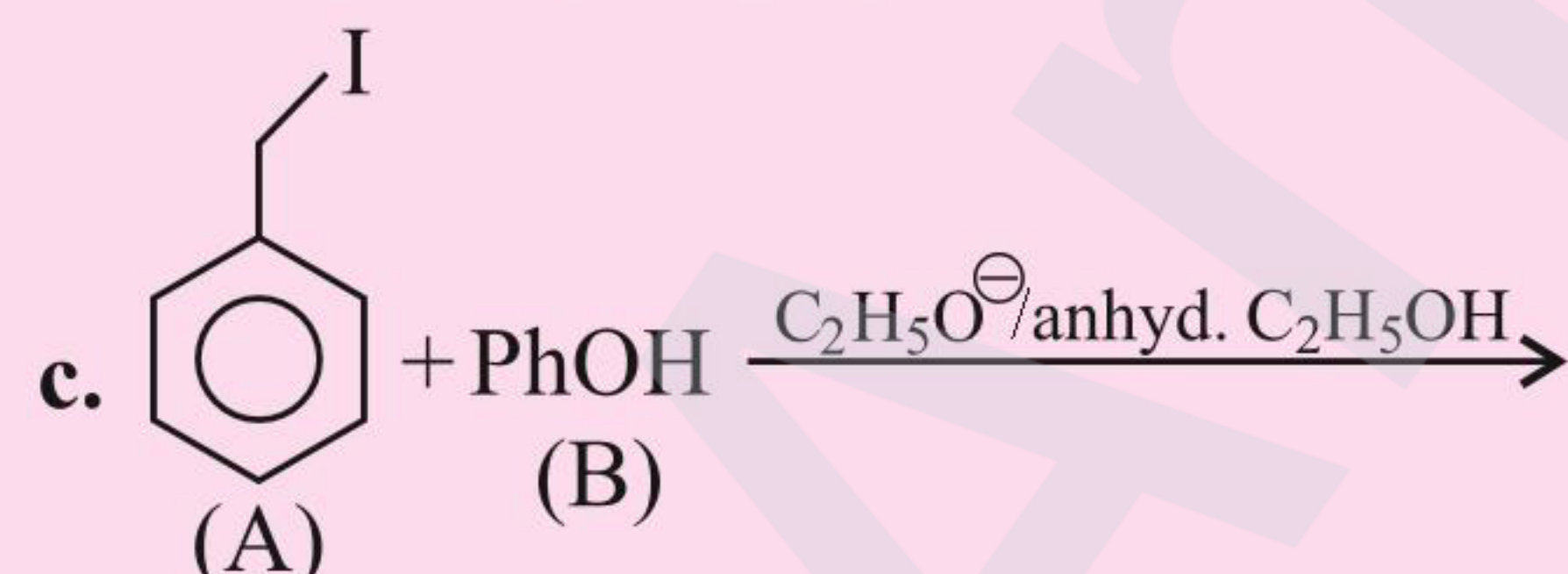


- i. PhOC_2H_5
iii. PhI

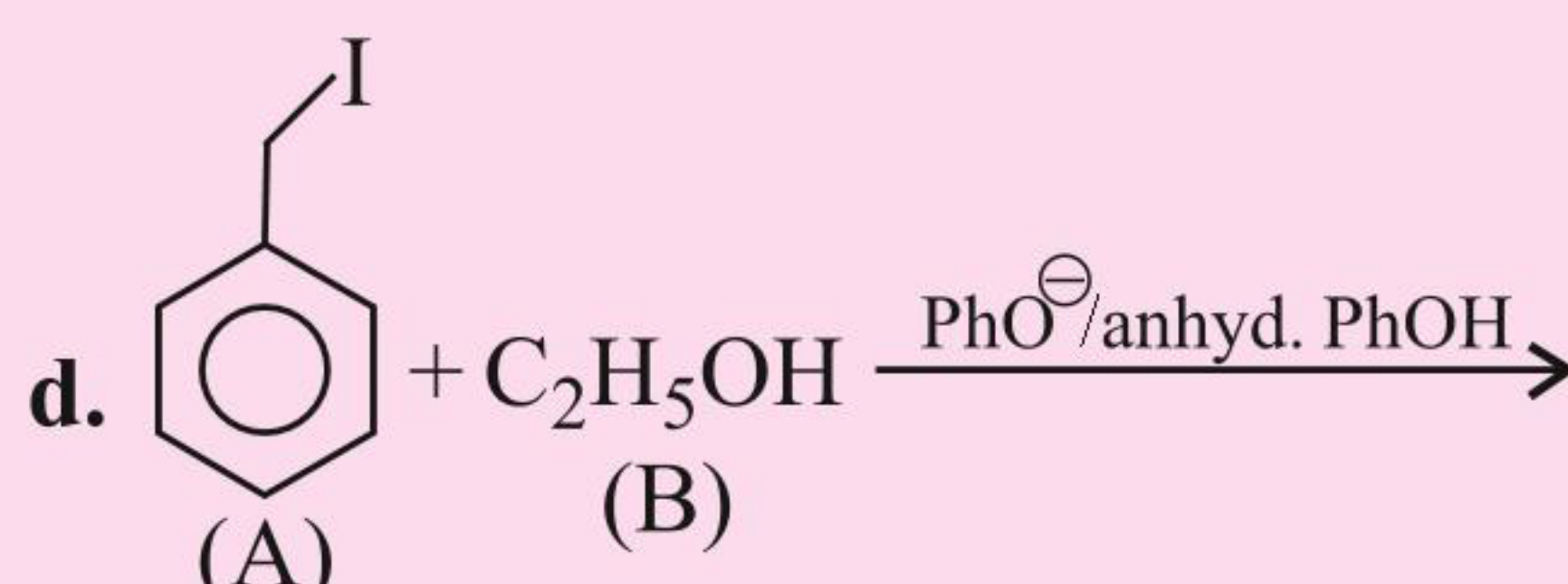
- ii. $\text{Ph}-\text{O}-\text{Ph}$
iv. $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$



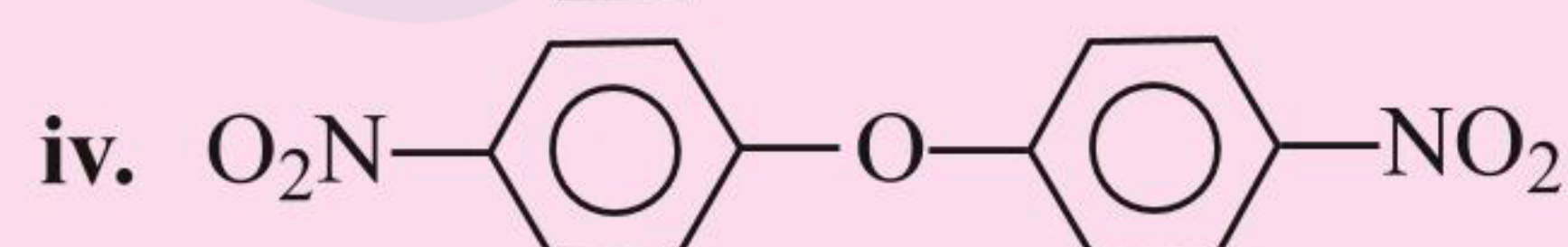
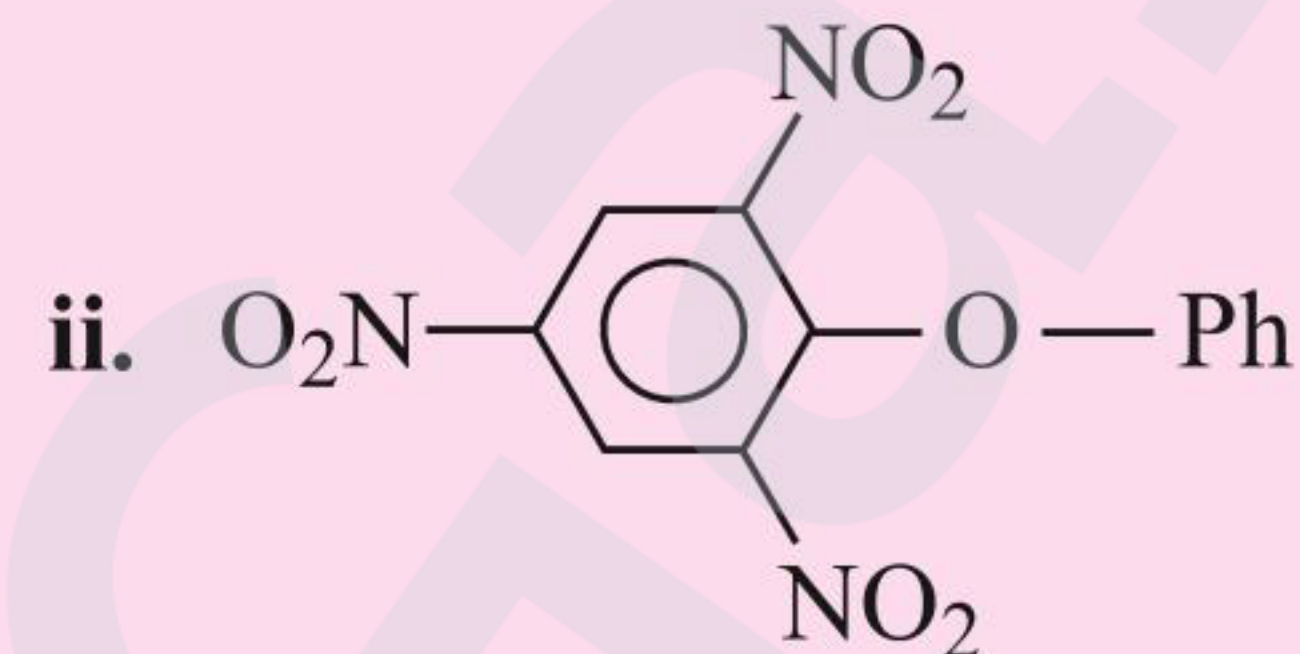
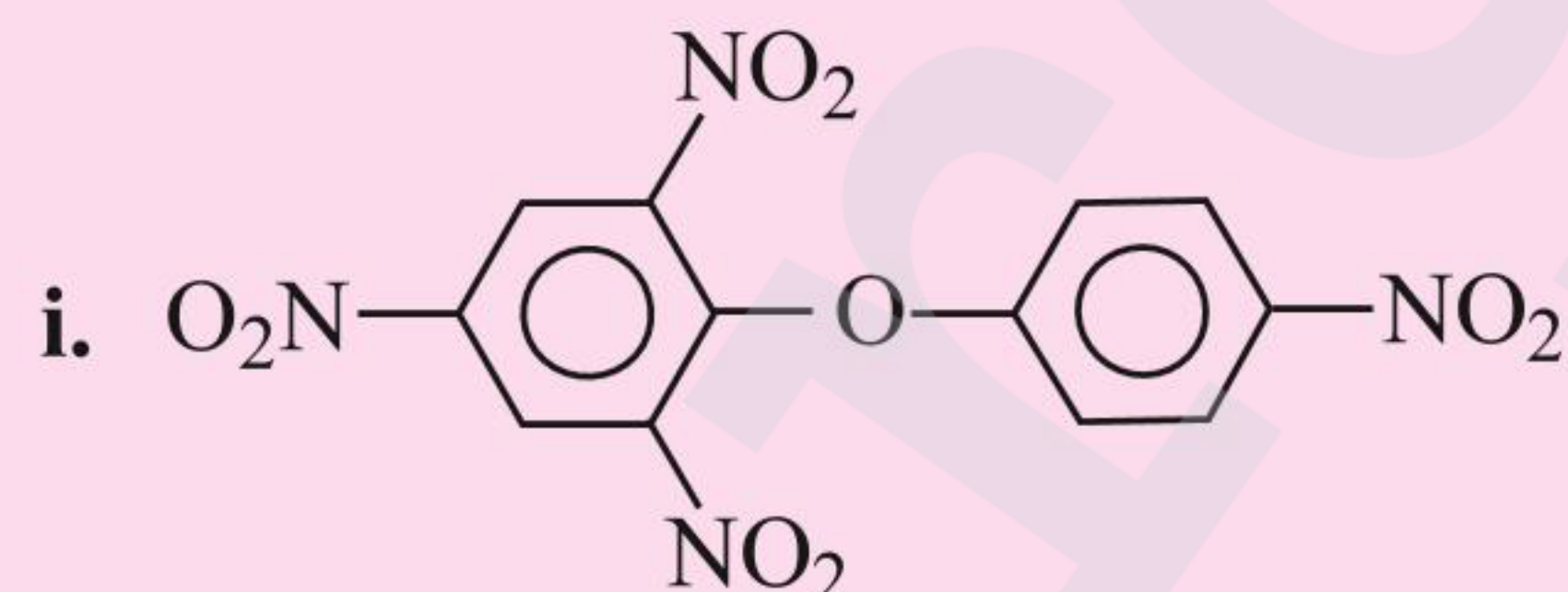
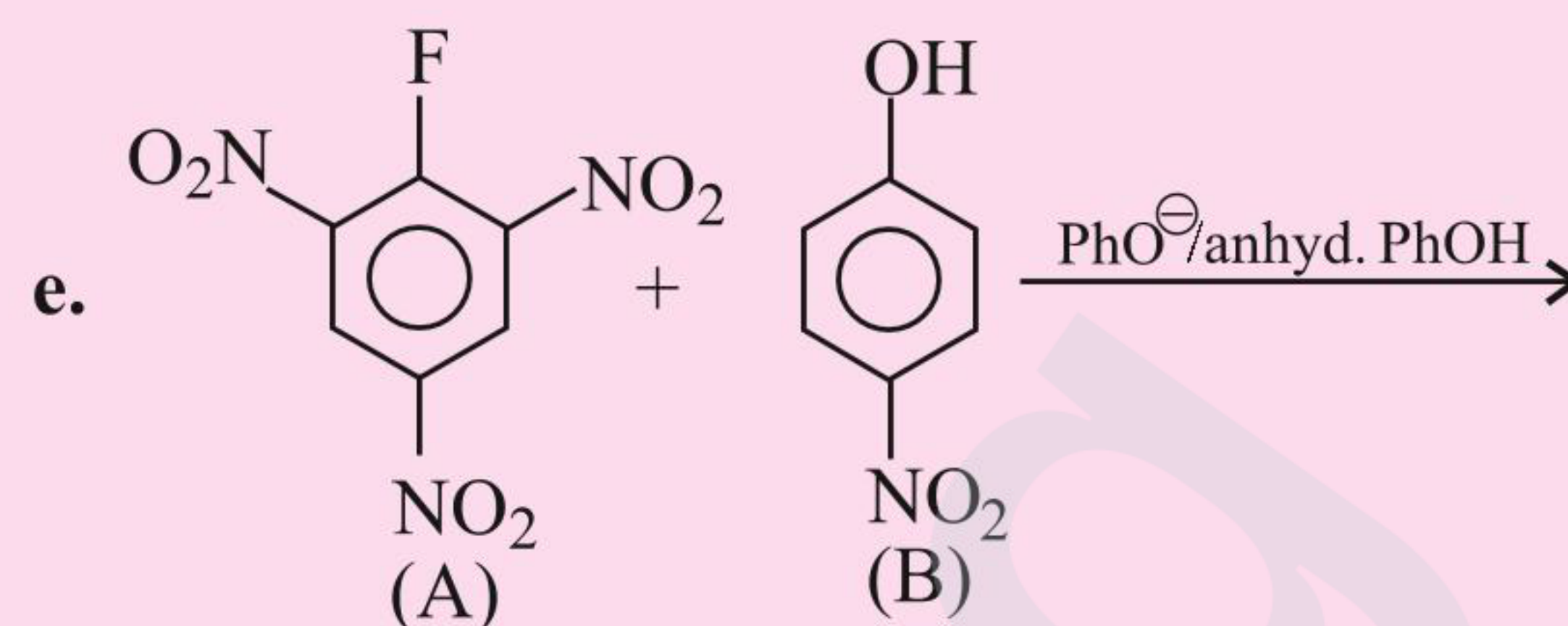
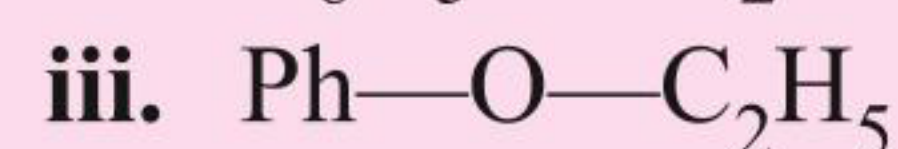
- i. $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-OC}_2\text{H}_5$
ii. $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-NO}_2$
iii. $\text{C}_2\text{H}_5\text{-O-CH}_3$
iv. $p\text{-NO}_2\text{-C}_6\text{H}_5\text{-I}$



- i. $\text{C}_6\text{H}_5\text{CH}_2\text{-O-Ph}$
ii. $\text{C}_6\text{H}_5\text{CH}_2\text{-O-C}_2\text{H}_5$
iii. $\text{Ph-O-C}_2\text{H}_5$
iv. $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$

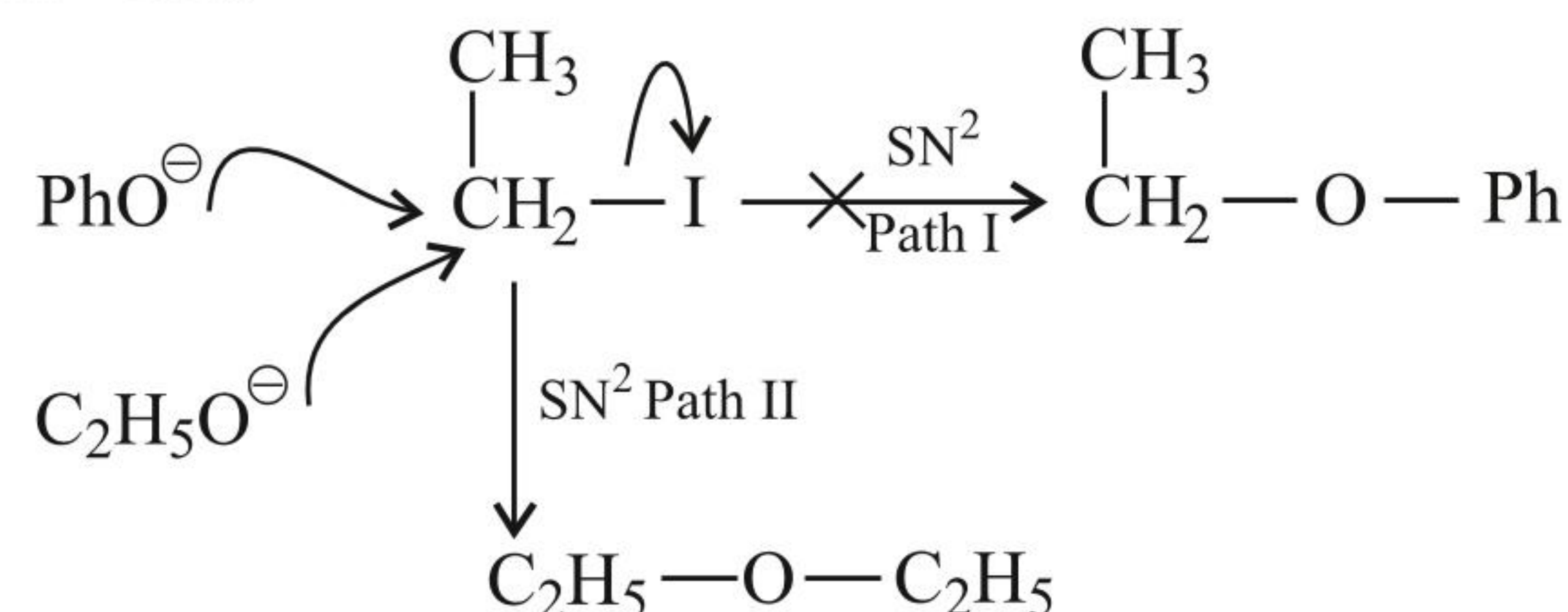


- i. $\text{C}_6\text{H}_5\text{CH}_2\text{-O-C}_2\text{H}_5$



Sol.

a. iv. $\text{C}_2\text{H}_5\text{O}^-$ acts as a base. It abstracts H^+ from phenol to form PhO^- ion.

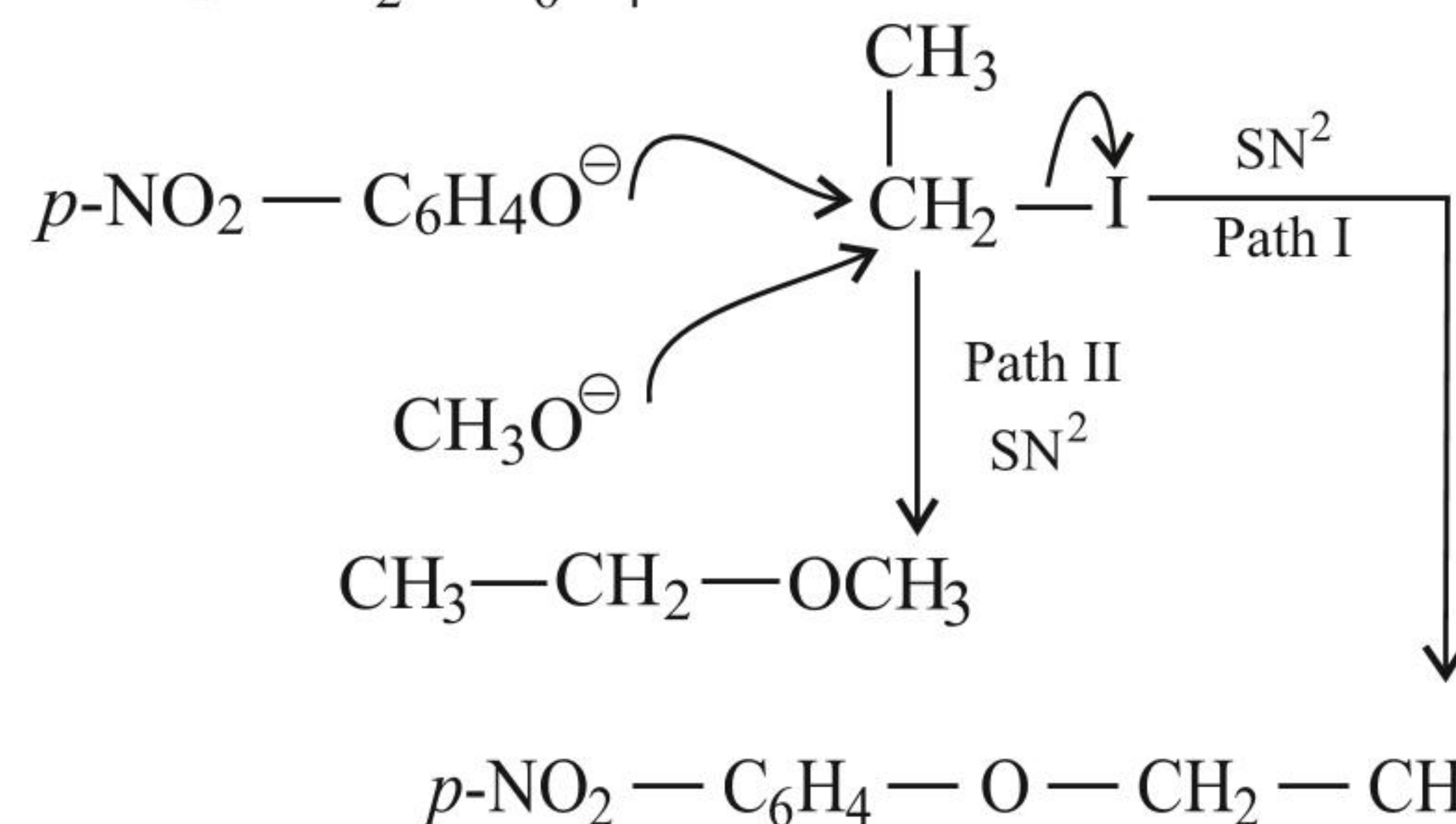


$\text{C}_2\text{H}_5\text{O}^-$ is a stronger nucleophile than PhO^- . Hence, the product is obtained by path II.

(Acidic character: $\text{PhOH} > \text{C}_2\text{H}_5\text{OH}$.)

(Basic and nucleophilic character: $\text{PhO}^- < \text{C}_2\text{H}_5\text{O}^-$)

b. iii. CH_3O^- acts as a base. It abstracts H^+ from p -nitrophenol to form $p\text{-NO}_2\text{-C}_6\text{H}_4\text{O}^-$.

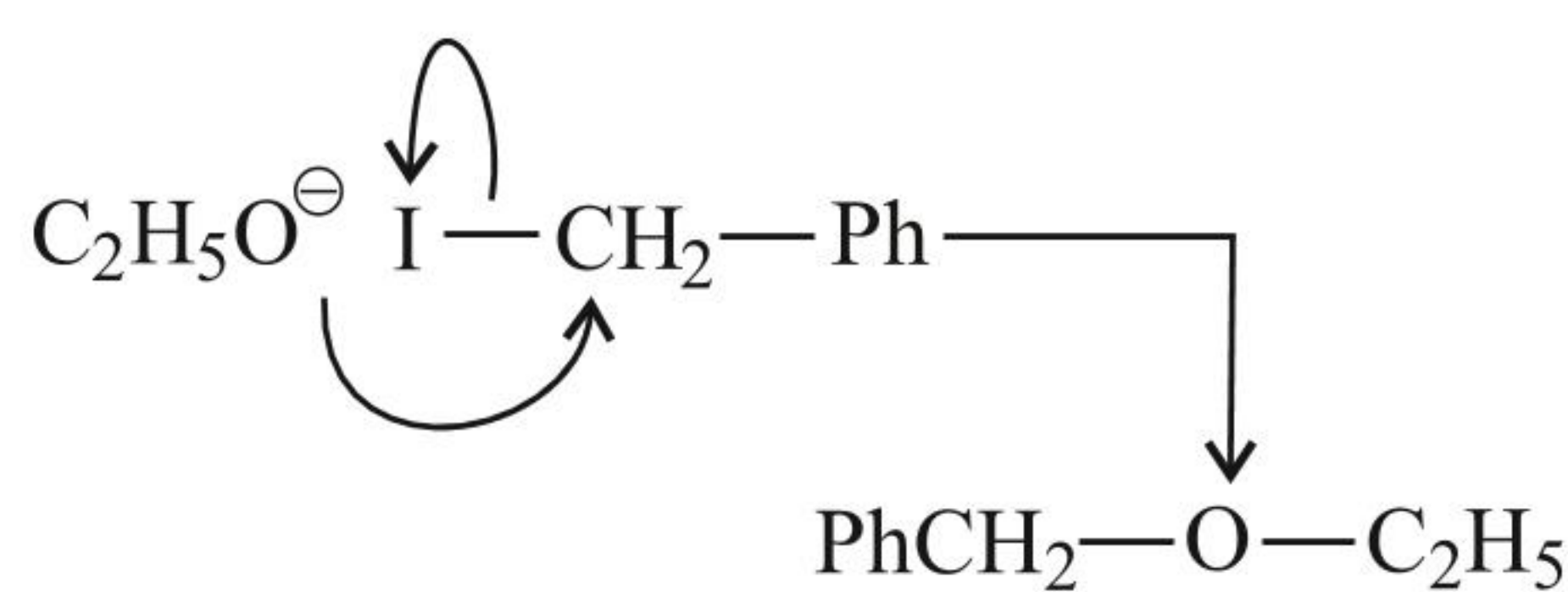


CH_3O^- is a stronger nucleophile than $p\text{-NO}_2\text{-C}_6\text{H}_4\text{O}^-$, hence the product is obtained by path II.

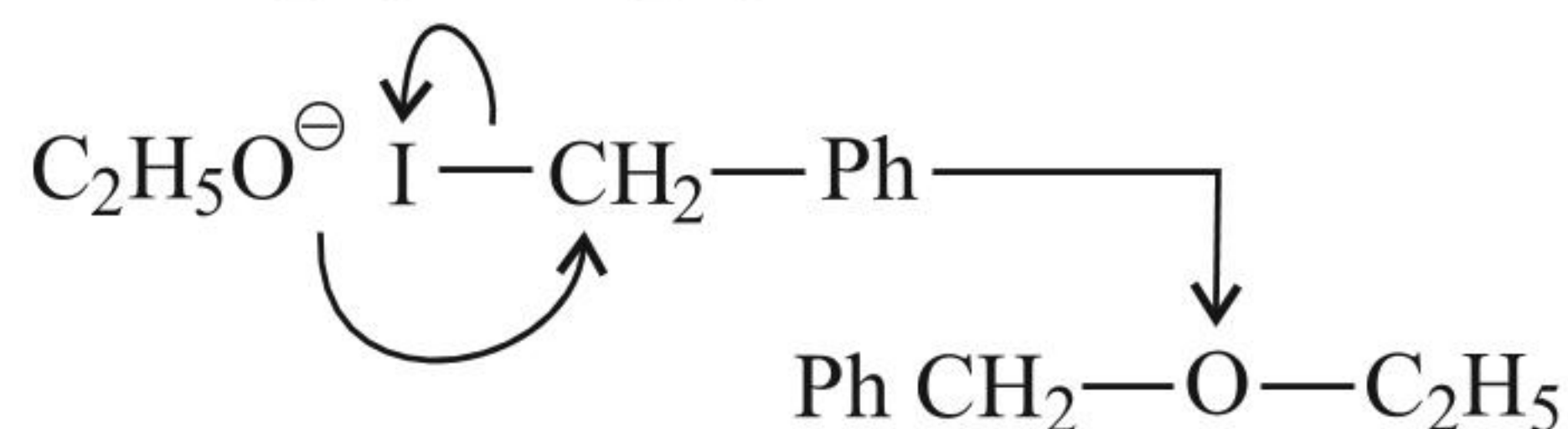
(Acidic character: $p\text{-NO}_2\text{-C}_6\text{H}_4\text{OH} > \text{CH}_3\text{OH}$.)

(Basic and nucleophilic character: $p\text{-NO}_2\text{-C}_6\text{H}_4\text{O}^- < \text{CH}_3\text{O}^-$)

c. ii. $\text{C}_2\text{H}_5\text{O}^-$ acts as a base. It abstracts H^+ from PhOH to form PhO^- ion. $\text{C}_2\text{H}_5\text{O}^-$ is a stronger nucleophile than PhO^- .



- d. i. PhO^\ominus acts as a base and it abstracts H^\oplus from $\text{C}_2\text{H}_5\text{OH}$ to form $\text{C}_2\text{H}_5\text{O}^\ominus$. $\text{C}_2\text{H}_5\text{O}^\ominus$ is a stronger nucleophile than PhO^\ominus .



- e. ii. PhO^\ominus acts as a base and it abstracts H^\oplus from *p*-nitro phenol to give $\text{p-NO}_2\text{C}_6\text{H}_5\text{O}^\ominus$. PhO^\ominus is stronger nucleophile than $\text{p-NO}_2\text{C}_6\text{H}_5\text{O}^\ominus$.

(Acidic character: $\text{p-NO}_2\text{C}_6\text{H}_5\text{OH} > \text{PhOH}$)

(Basic and nucleophilic character: $\text{p-NO}_2\text{C}_6\text{H}_5\text{O}^\ominus < \text{PhO}^\ominus$)

Moreover, strong EWG in (A) favours ArSN reaction.

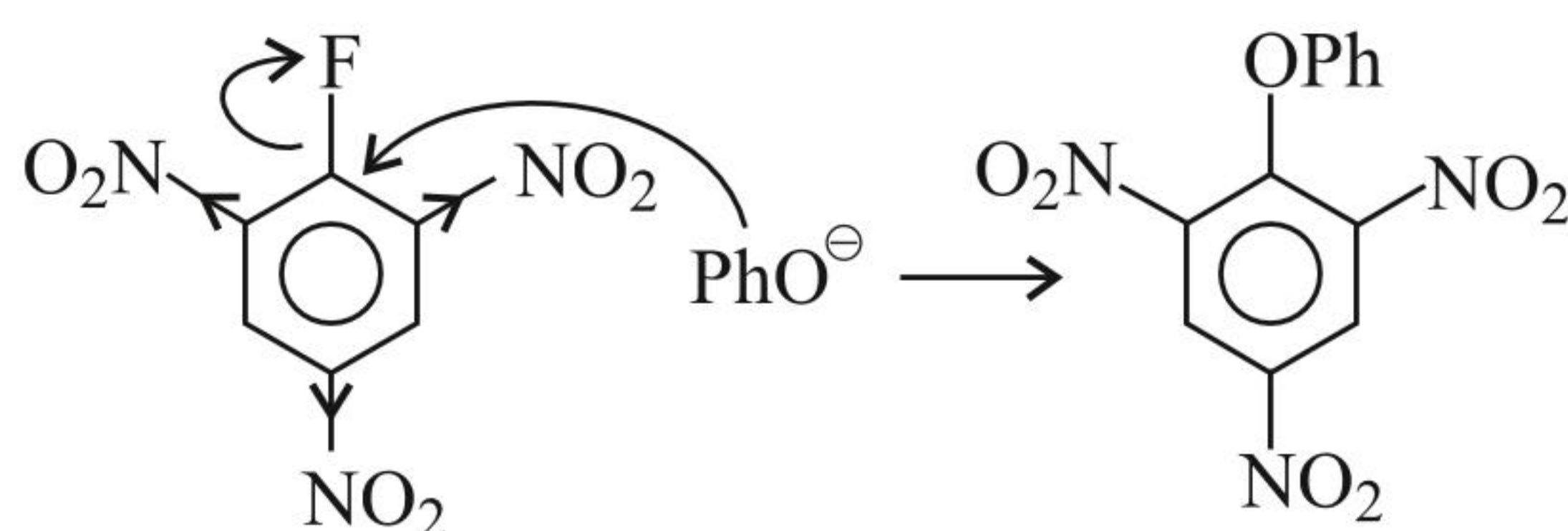
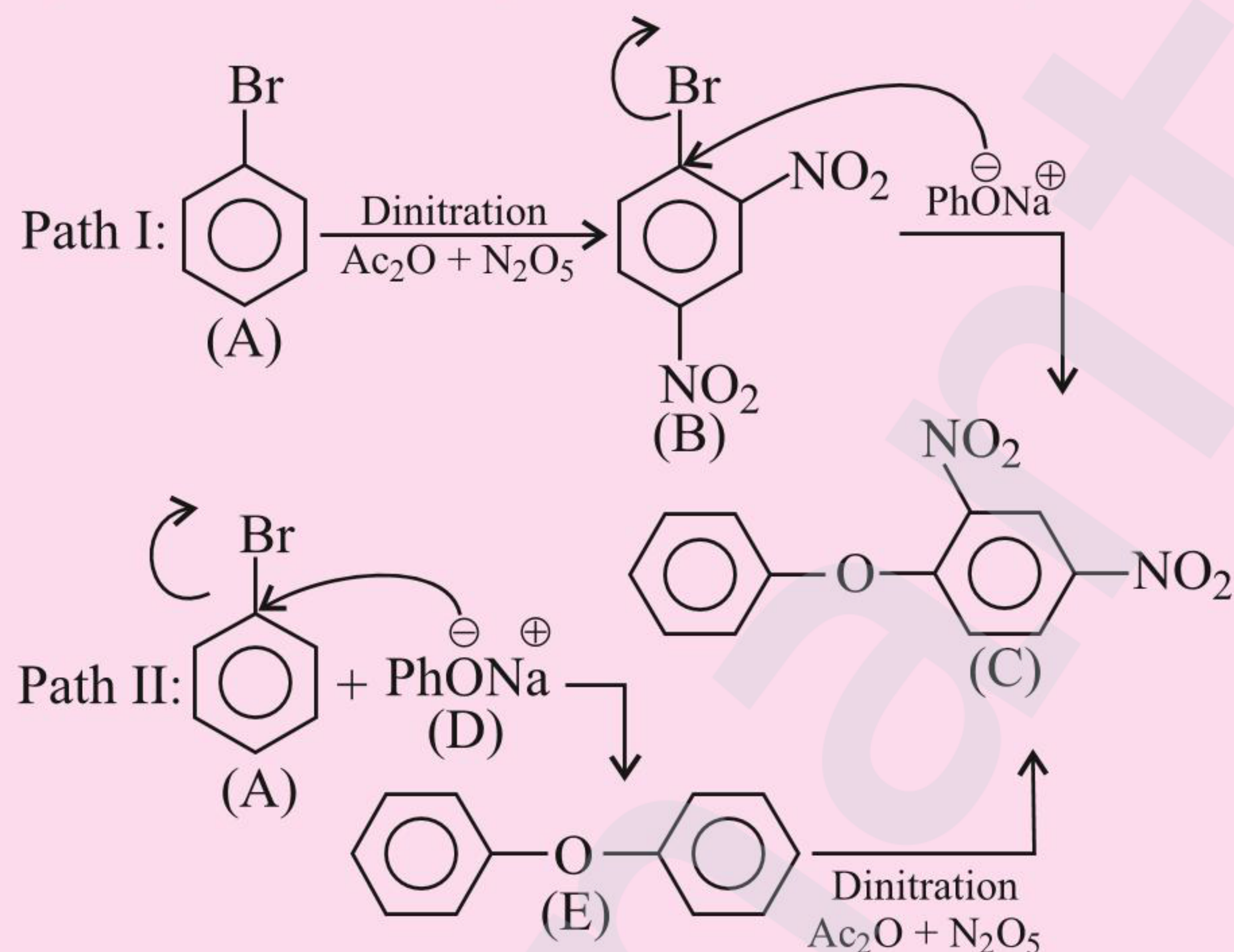


ILLUSTRATION 4.29

There are two paths for the preparation of phenyl-2,4-dinitro phenyl ether (C). Which path is feasible and why?



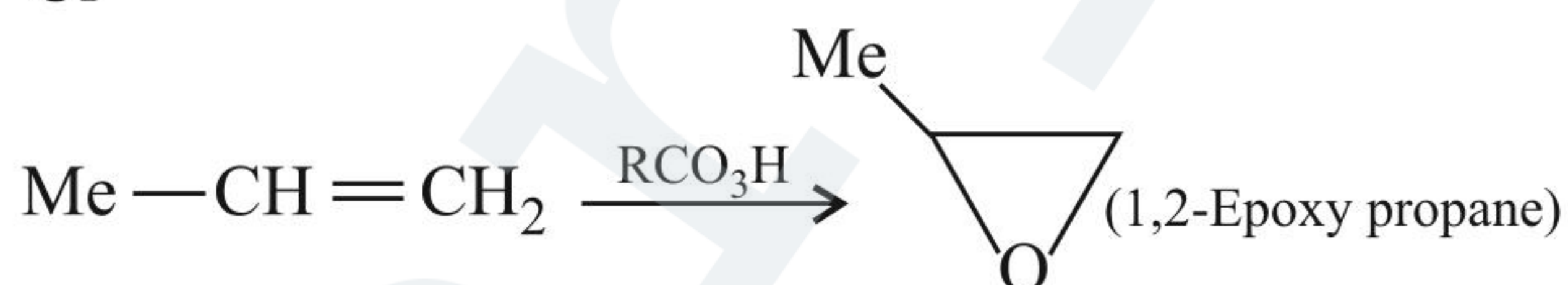
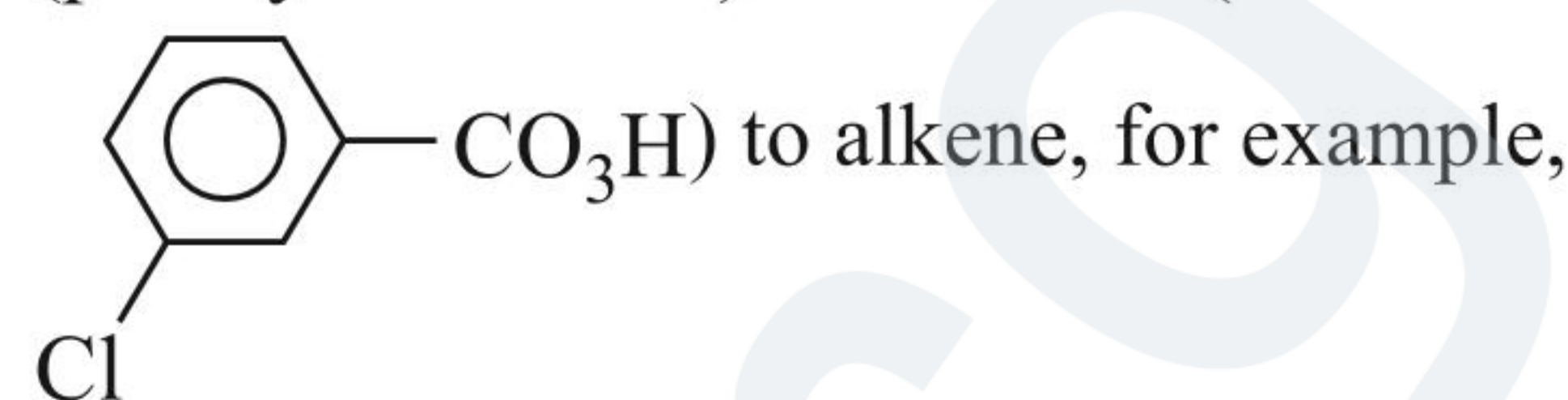
Sol.

- Path I is feasible. ArSN reaction (Williamson's synthesis) of nucleophile PhO^\ominus with (B) is feasible. Also, Br of (B) is activated by the two EWG ($-\text{NO}_2$) groups.
- Path II is not feasible. ArSN reaction of the nucleophile PhO^\ominus with (A) is not feasible because no activating group is present in (A).
- Dinitration of (E) does not give (C) but it gives $\text{O}_2\text{N-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-NO}_2$ because the first nitro group is deactivating so that second nitro group enters the other ring at *p*-position.

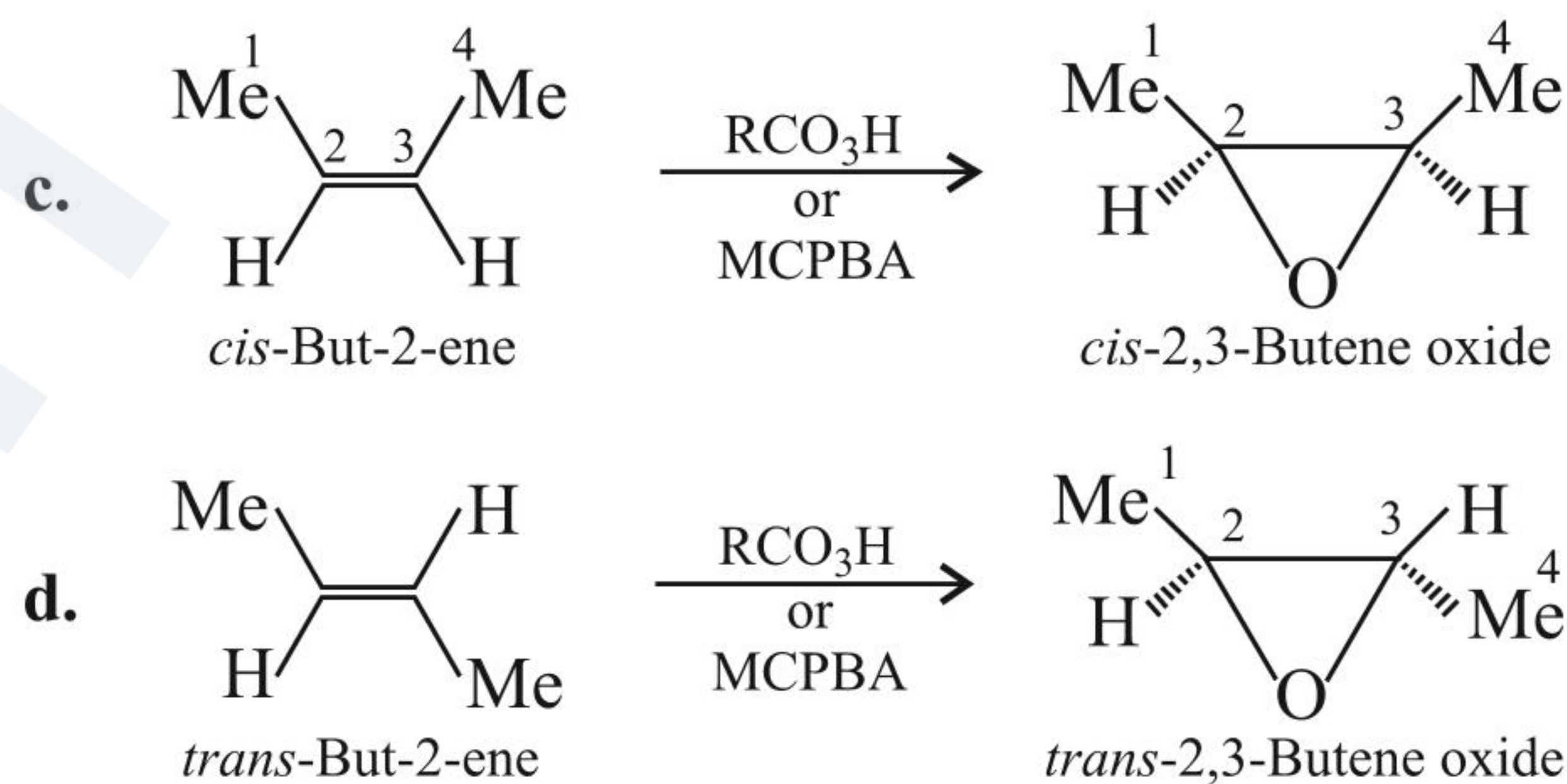
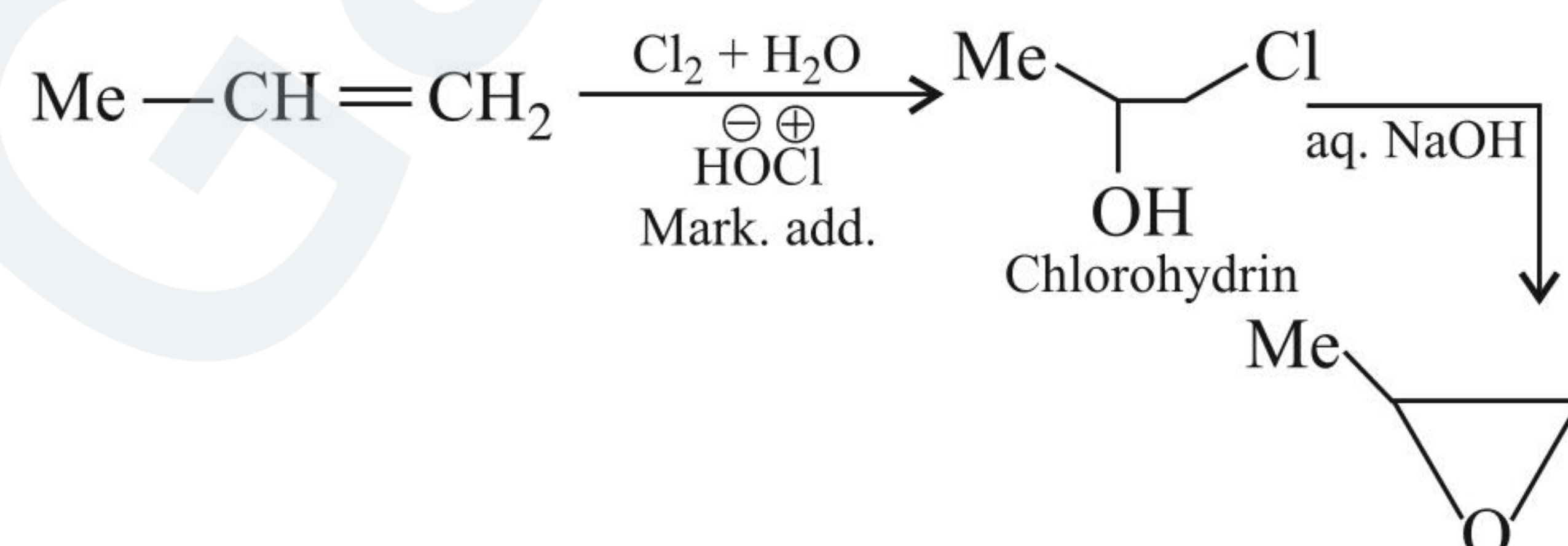
4.38 EPOXIDES (OXIRANES)

- a. Epoxides are prepared by adding a peroxyacid

$\left(\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{H} \right)$ or $\text{F}_3\text{C}-\text{COOH}$ (trifluoroacetic acid) or PhCO_3H (peroxy benzoic acid) or MeCO_3H (peroxy acetic acid) or MCPBA (*m*-chloro-perbenzoic acid

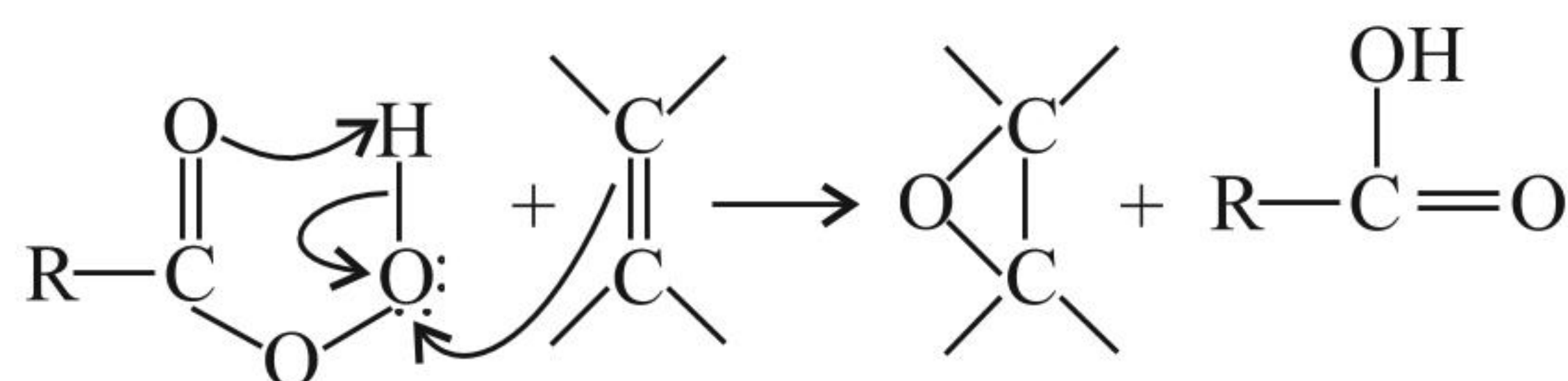


- b. Epoxides are also prepared by adding $(\text{Cl}_2 + \text{H}_2\text{O})$ to alkene followed by reaction with aq. NaOH.

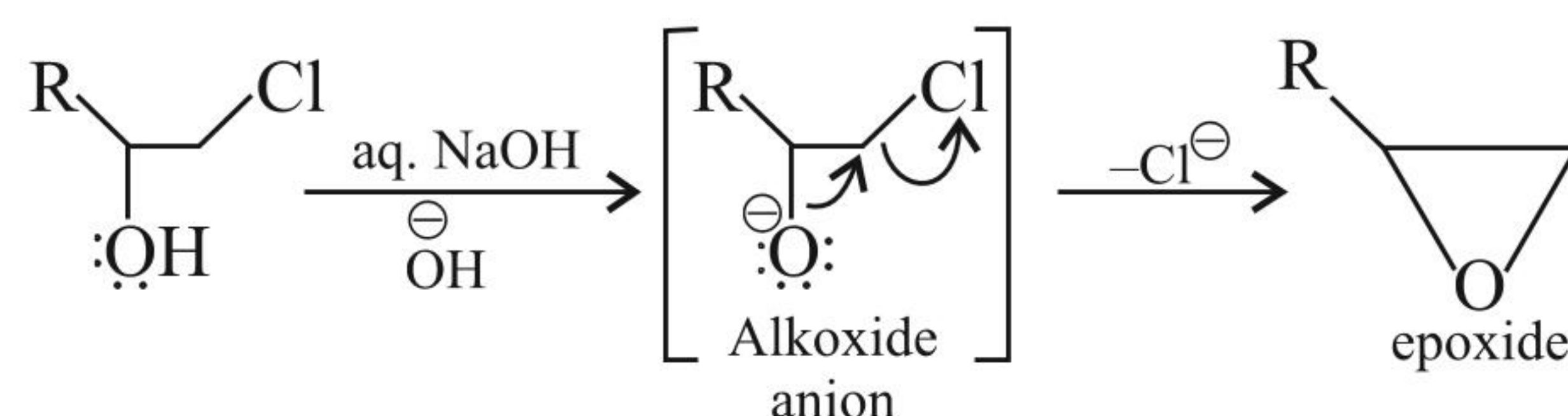


The stereochemistry of the alkene is retained in the epoxide. The reaction is stereospecific.

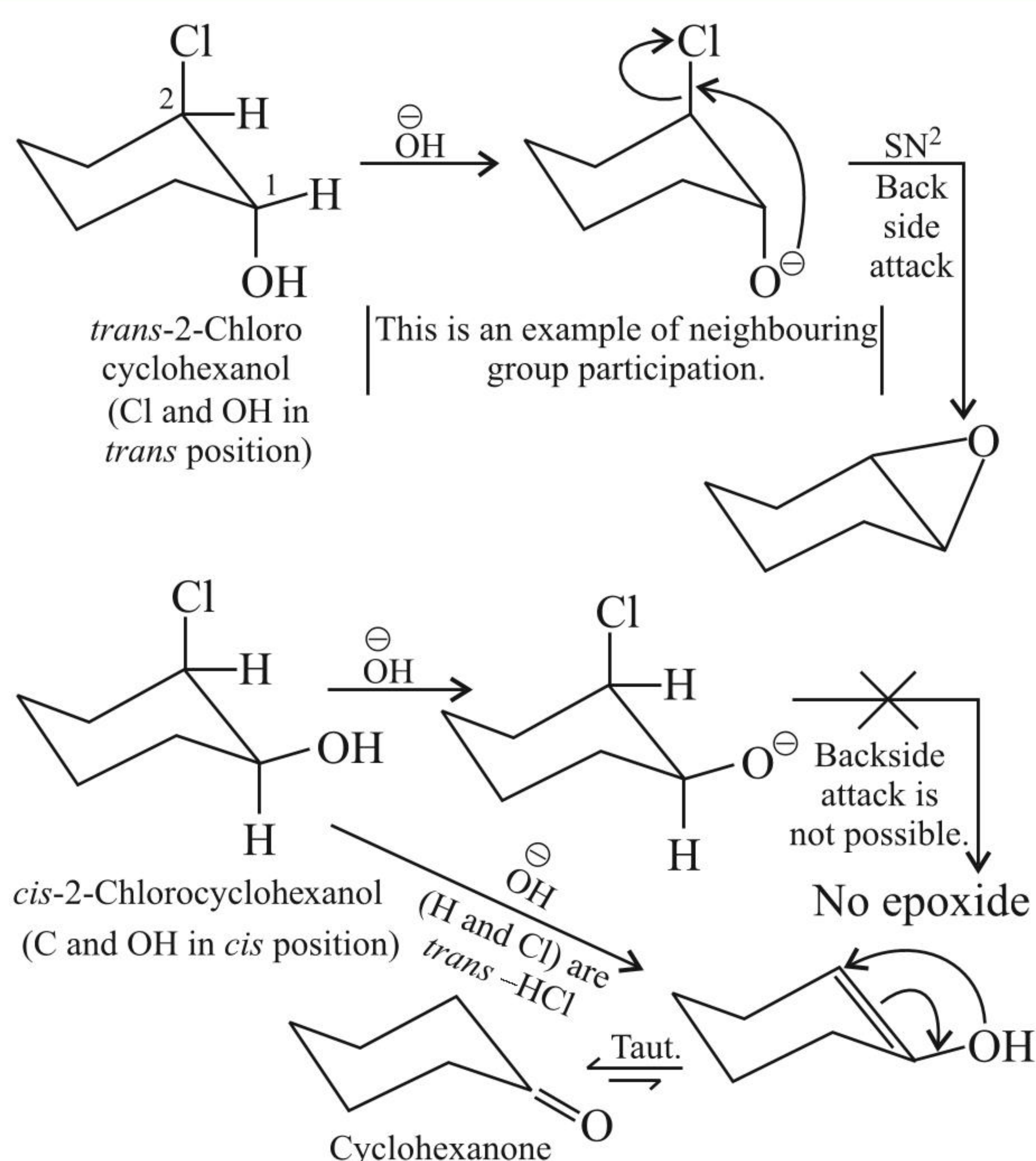
- e. **Mechanism:** The reaction proceeds via $\text{S}_\text{N}2$ mechanism. The π \bar{e} 's of the $(\text{C}=\text{C})$ bond attack on the O atom of (OH) of the peroxy acid, with the elimination of RCOOH .



- f. **Mechanism:** Formation of epoxide from chlorohydrin

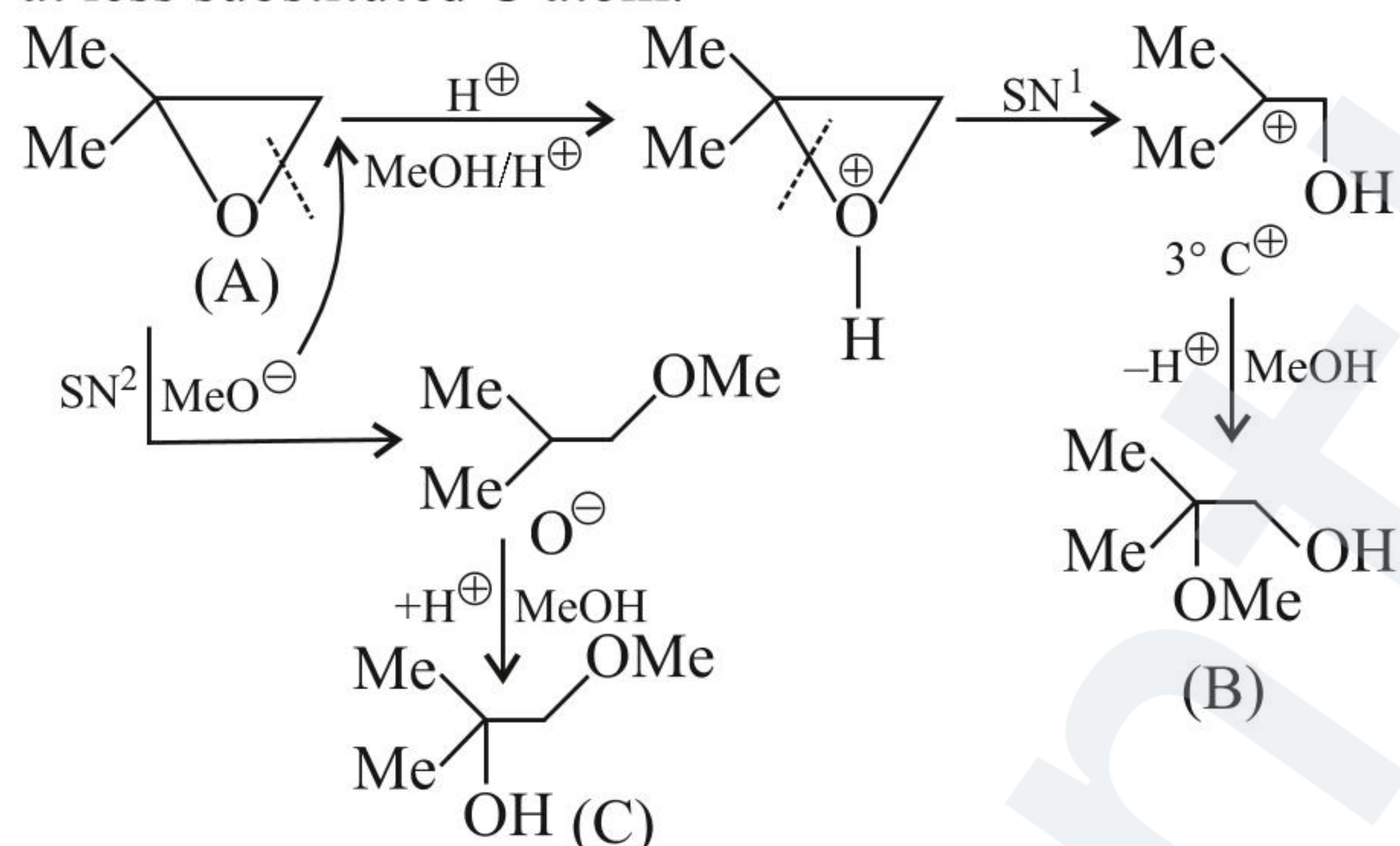


In $\text{S}_\text{N}2$ reaction, the nucleophile O^\ominus must attack from the back to displace Cl^\ominus . That is why *trans*-2-chlorocyclohexanol gives good yield of epoxy cyclohexane but *cis*-isomer does not form epoxide instead undergoes dehydrohalogenation reaction to give cyclohexanone.



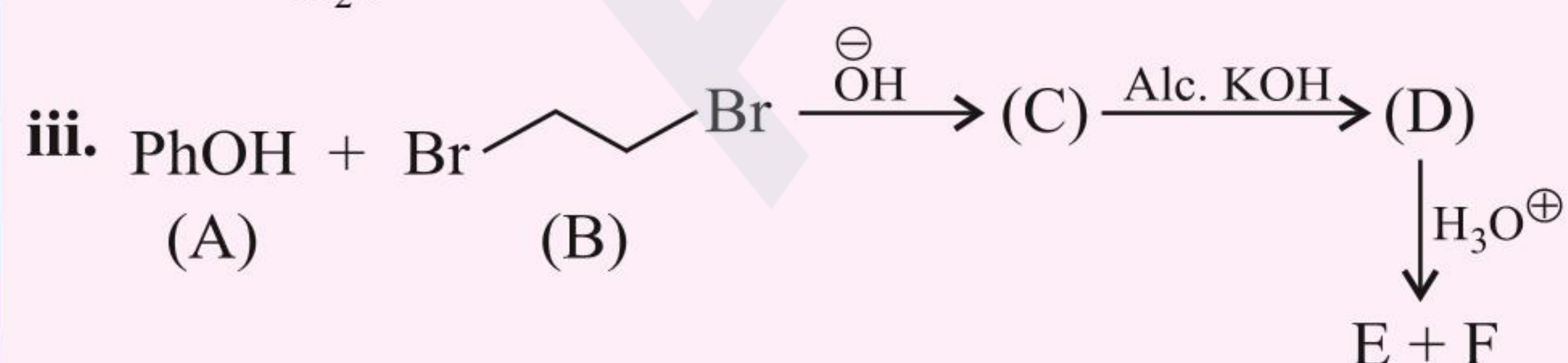
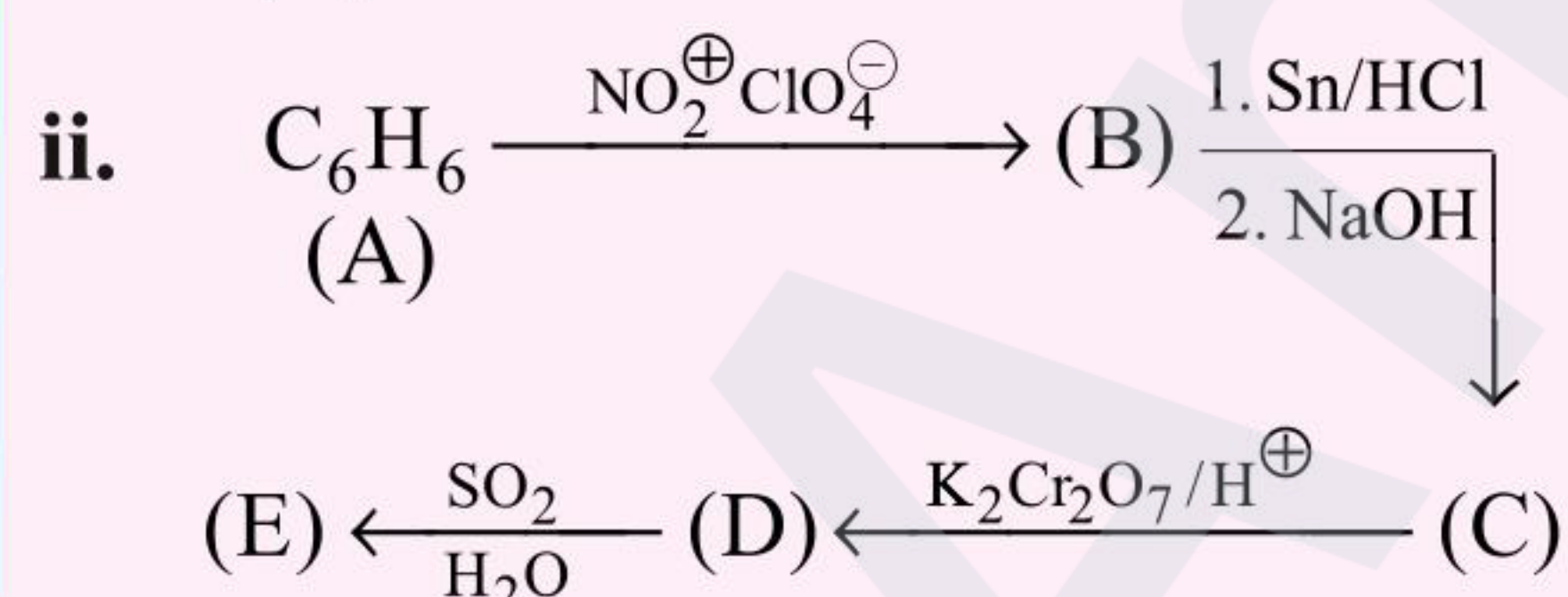
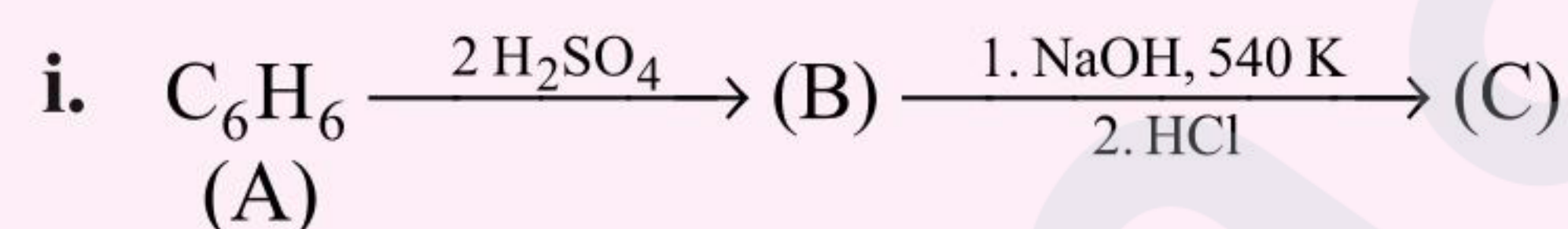
g. Acid-catalysed and base-catalysed reactions of epoxide:

Acid-catalysed reaction undergoes S_N1 -type ring opening to give $3^\circ C^+$ which is then bonded to ROH. Base-catalysed reaction undergoes by S_N2 mechanism with attack of ROH at less substituted C atom.

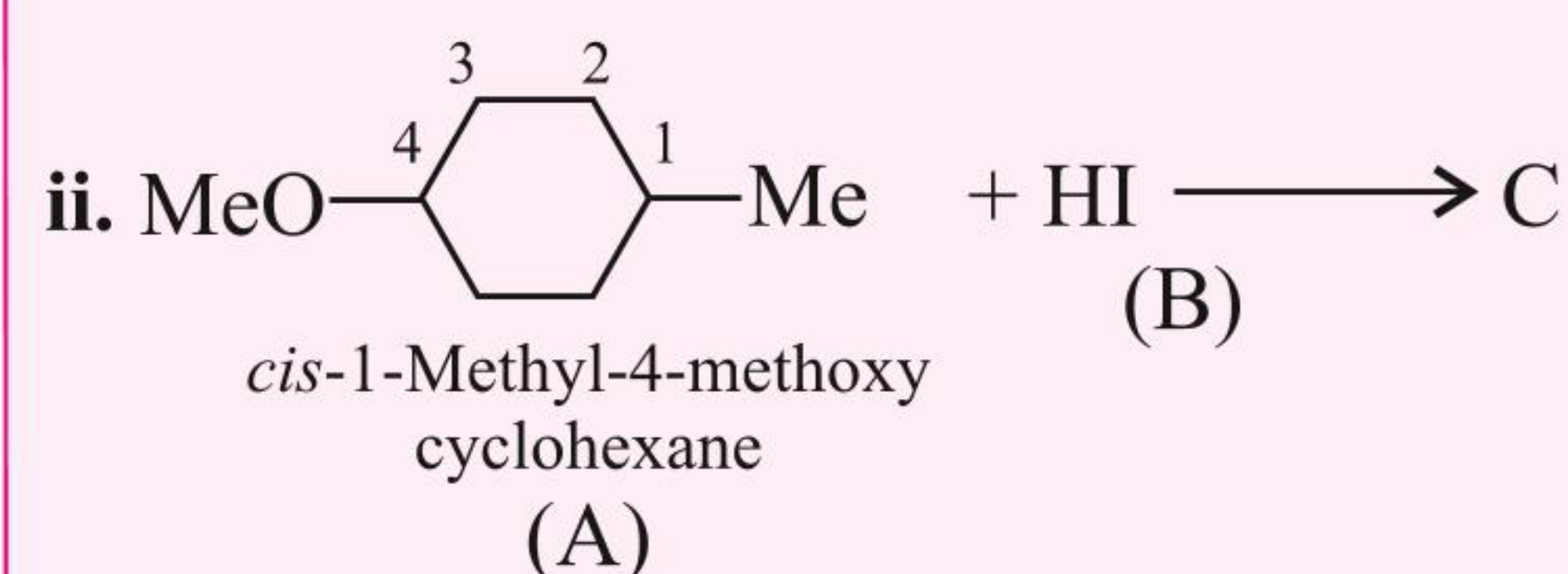
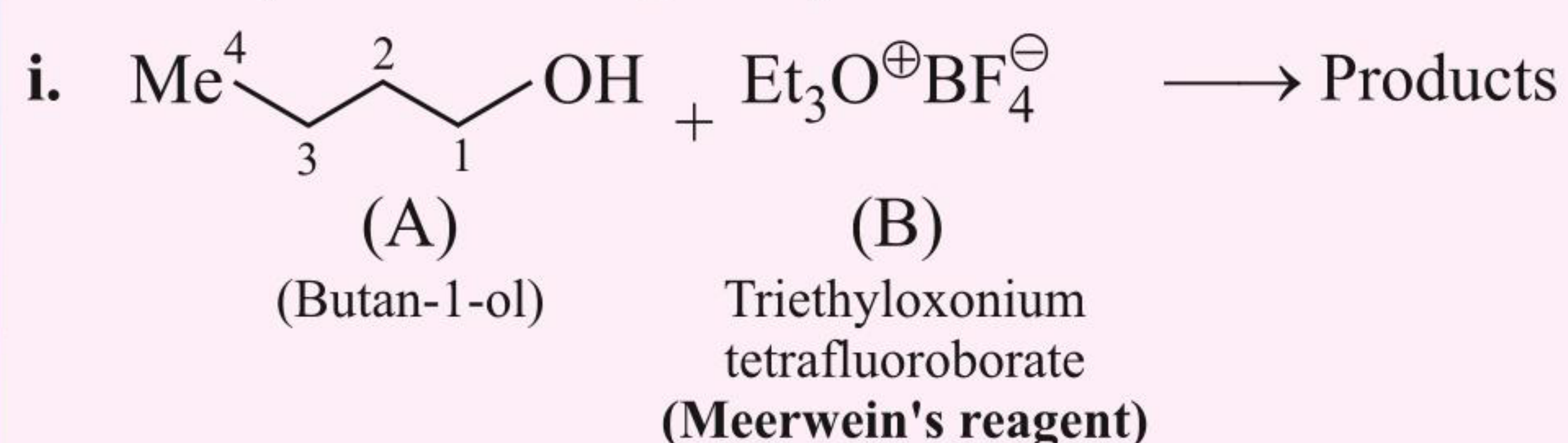


CONCEPT APPLICATION EXERCISE 4.2

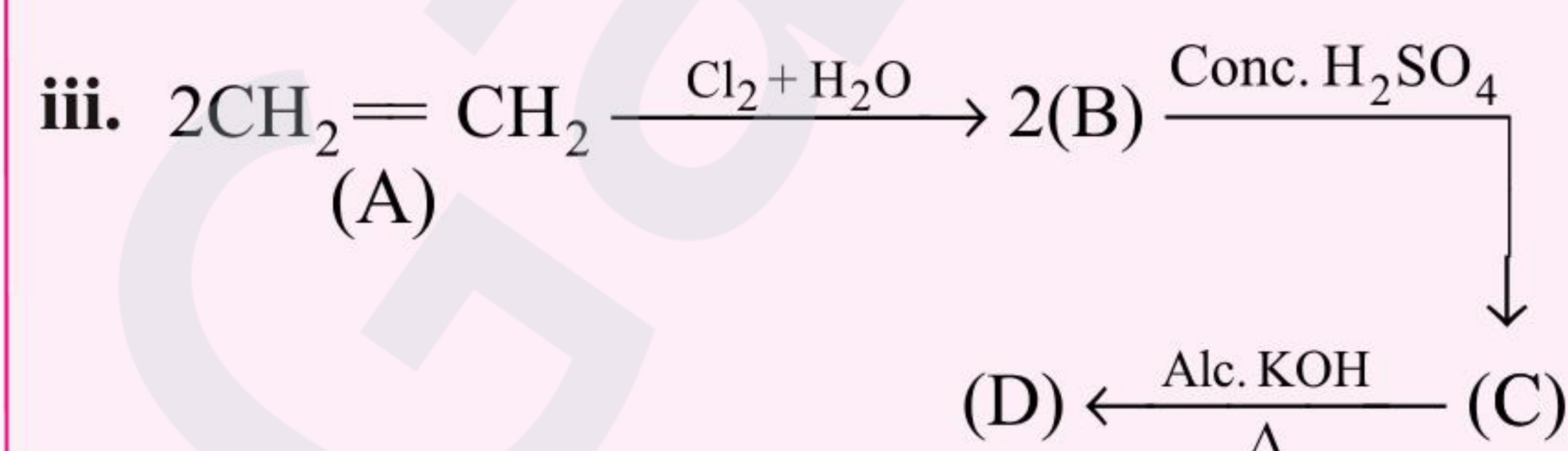
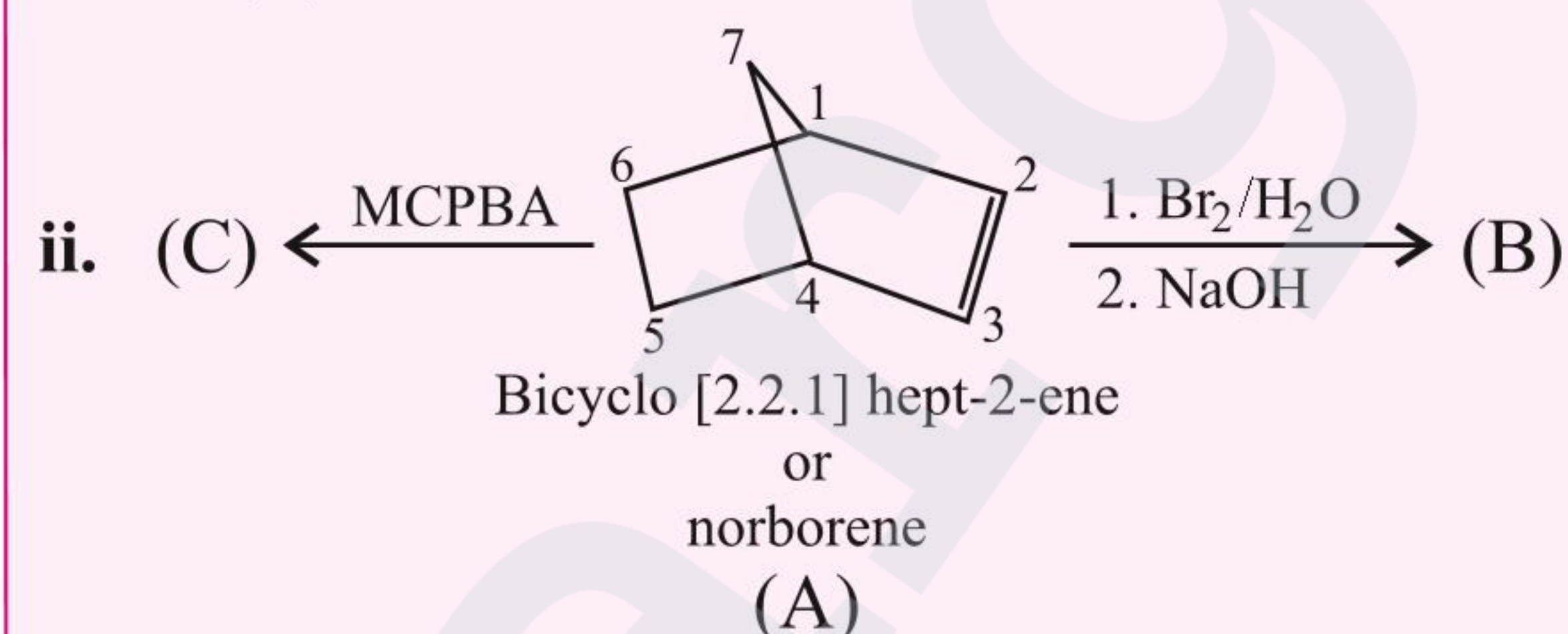
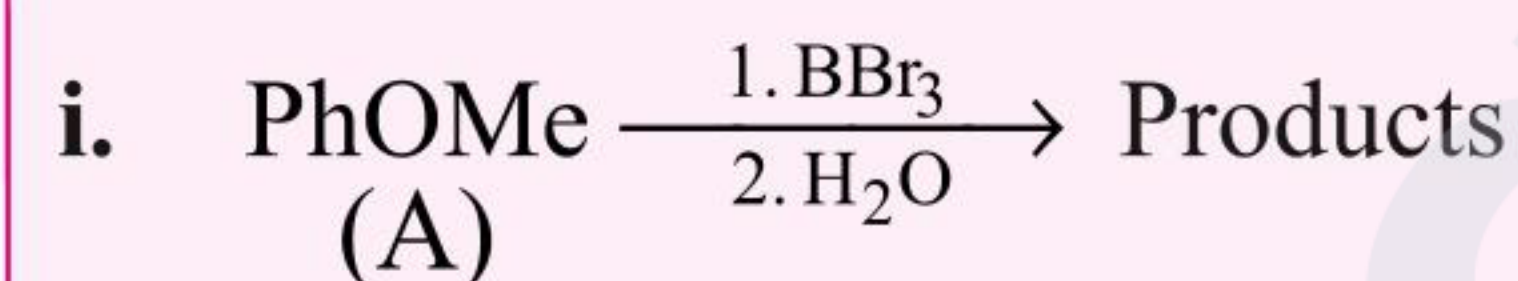
1. Identify the following compounds:



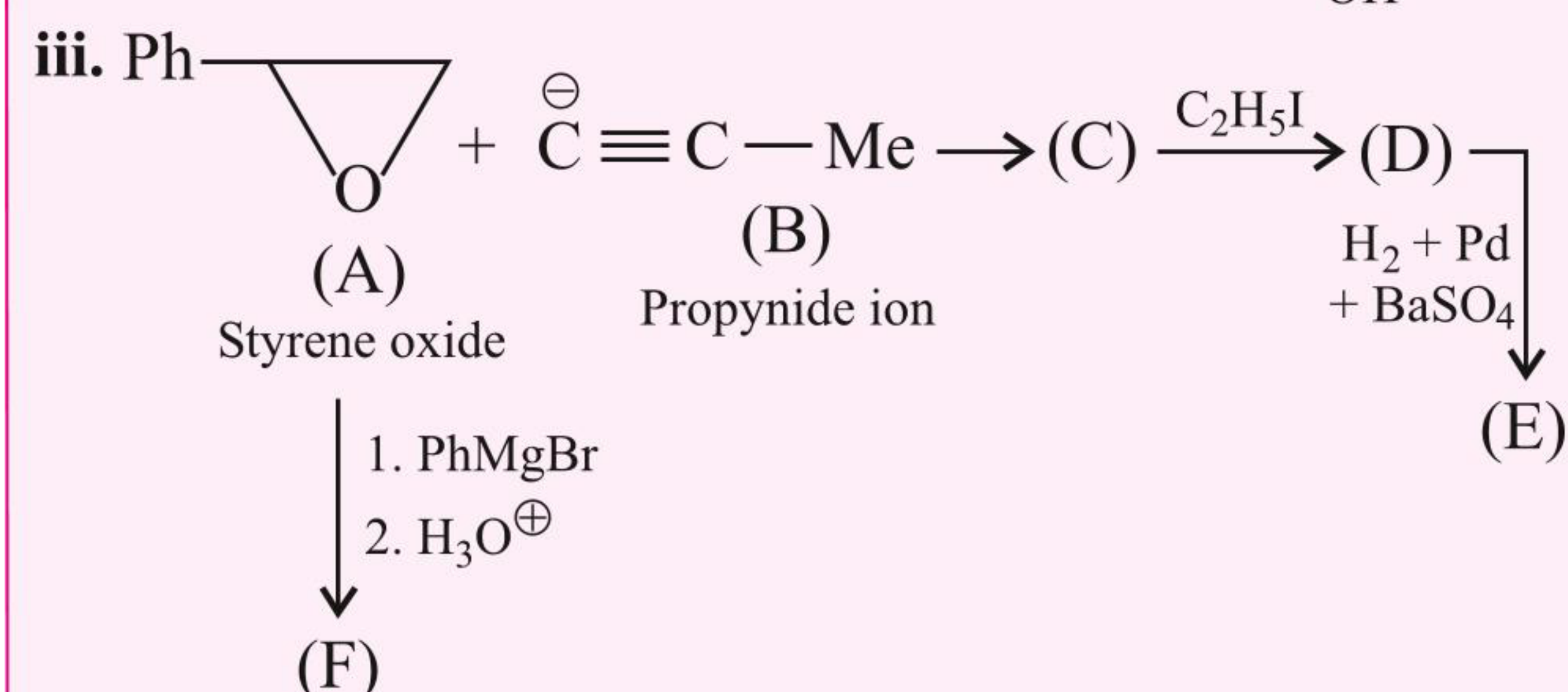
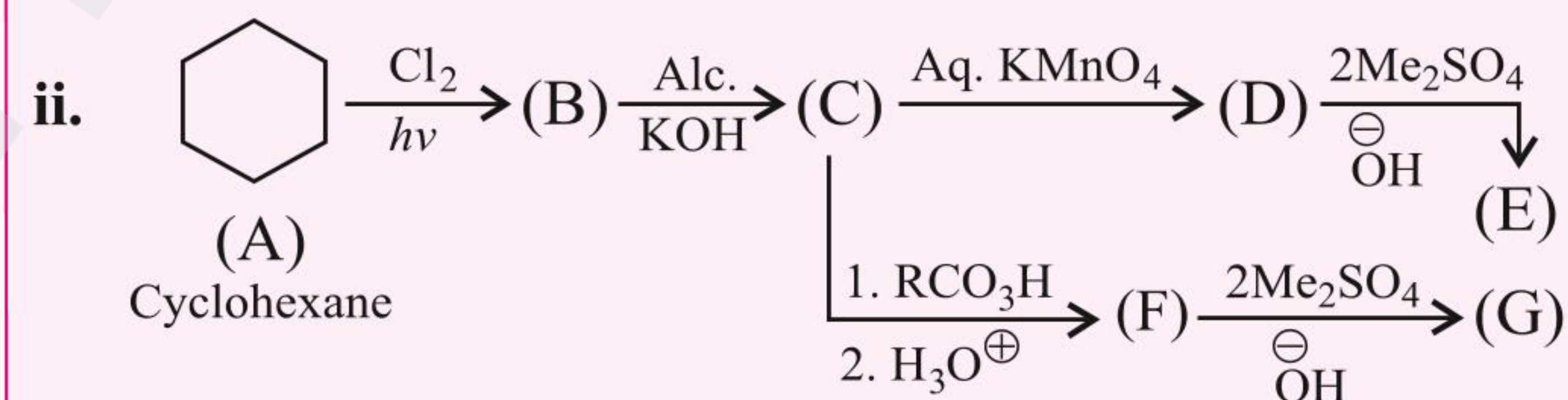
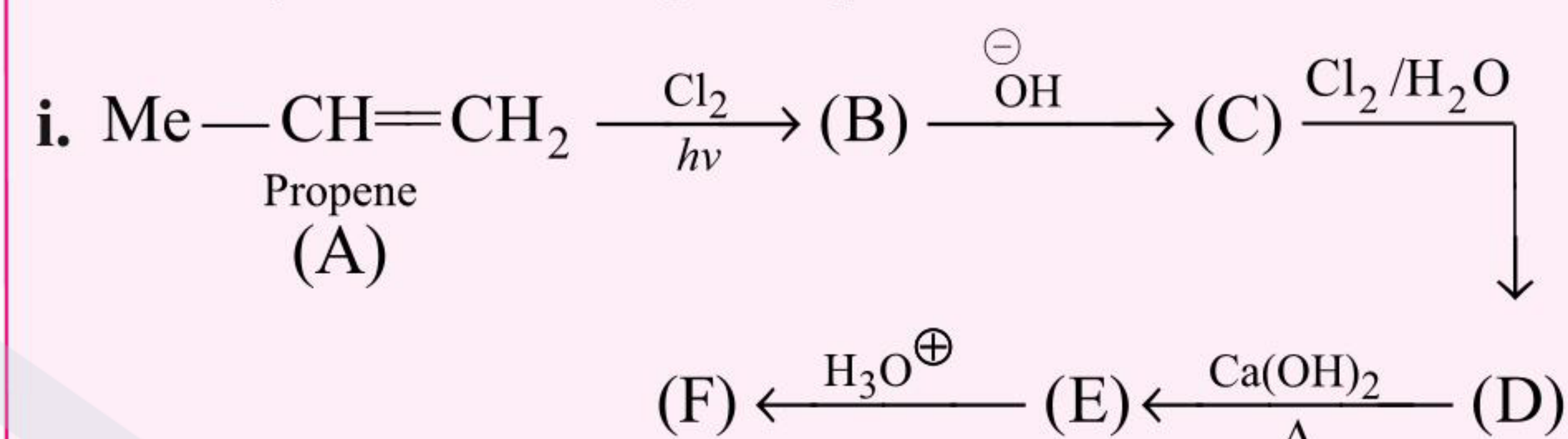
2. Identify the following compounds:



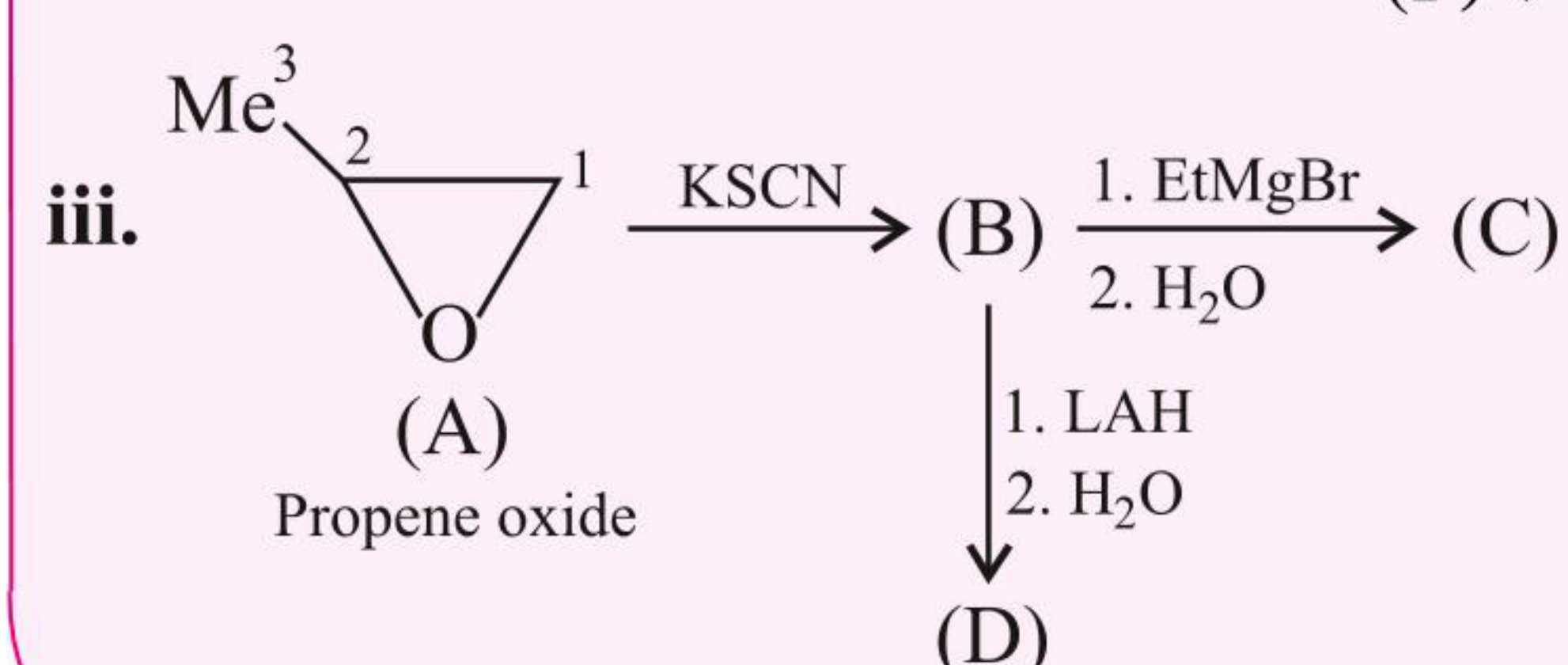
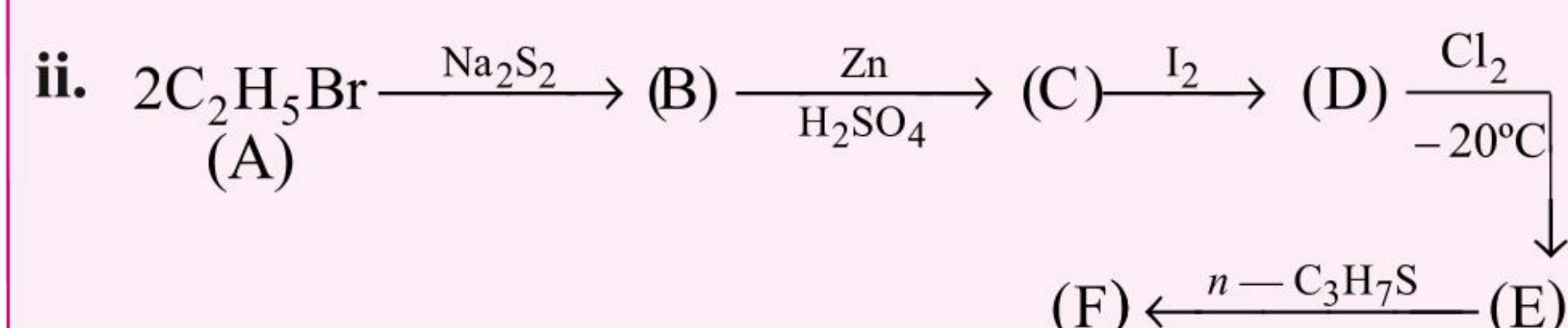
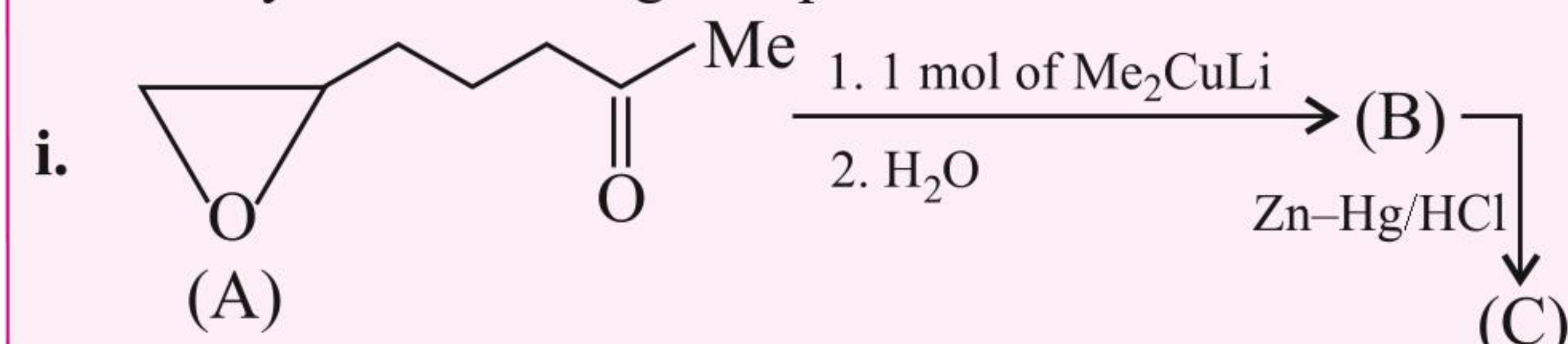
3. Identify the following compounds:



4. Identify the following compounds:



5. Identify the following compounds:



Exercises

Single Correct Answer Type

Alcohols and Phenols

1. The decreasing order of acidic character of the following is:

(I) EtOH

(II) Me—COOH

(III) MeOOC—CH₂—COOMe

(IV)

(1) II > III > IV > I

(2) II > III > I > IV

(3) I > IV > III > II

(4) IV > I > III > II

2. The decreasing order of acidic character of the following is:

(I)

(II)

(III)

(IV)

(1) II > IV > III > I

(2) I > III > IV > II

(3) IV > II > I > III

(4) III > I > II > IV

3. The decreasing order of acidic character of the following is:

(I)

(II)

(III) PhNH₂

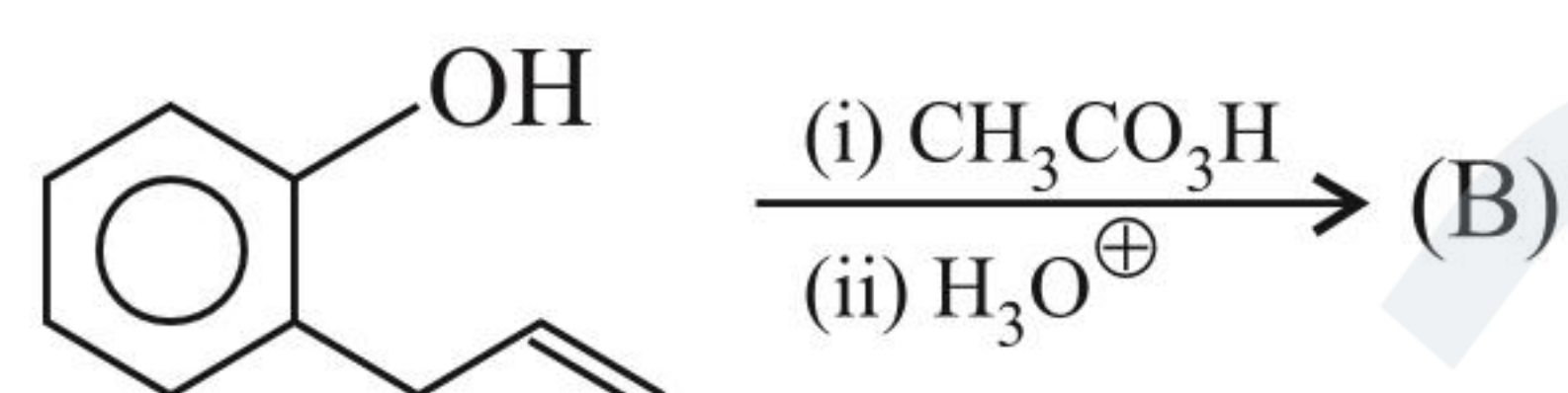
(1) II > I > III

(2) III > I > II

(3) II > III > I

(4) I > III > II

4. Consider the following reaction and identify (B).



(1)

(2)

(3)

(4)

5. Give the decreasing order of the reaction rates of the following compounds with HBr.

(I)

(II)

(III)

(IV)

(1) I > II > III > IV

(2) IV > III > II > I

(3) II > I > III > IV

(4) IV > III > I > II

6. Give the decreasing order of reactivity of the following compounds with HBr.

(I)

(II)

(III)

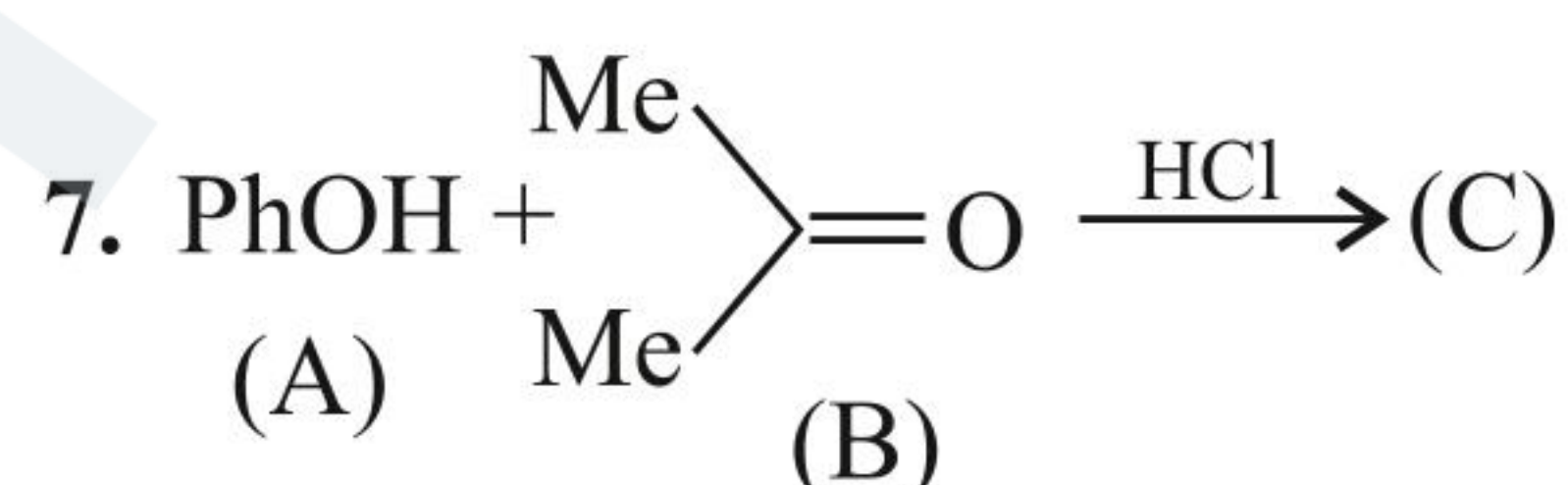
(IV)

(1) III > IV > II > I

(2) III > II > IV > I

(3) III > II > I > IV

(4) II > III > IV > I



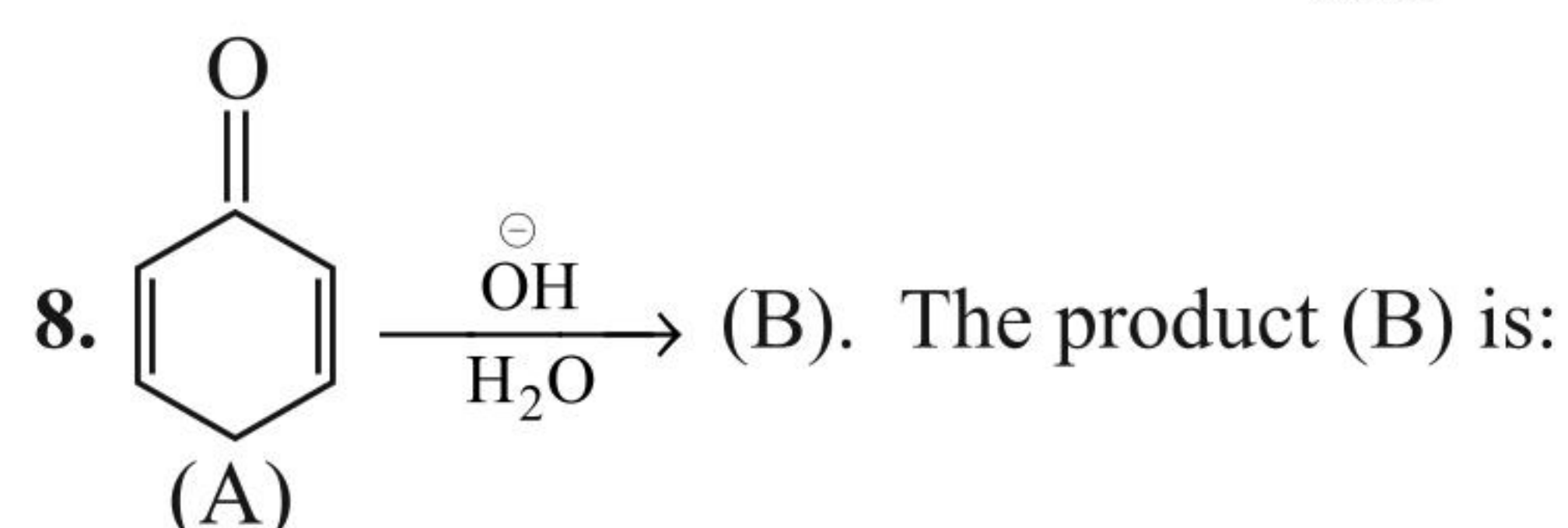
The compound (C) is:

(1)

(2)

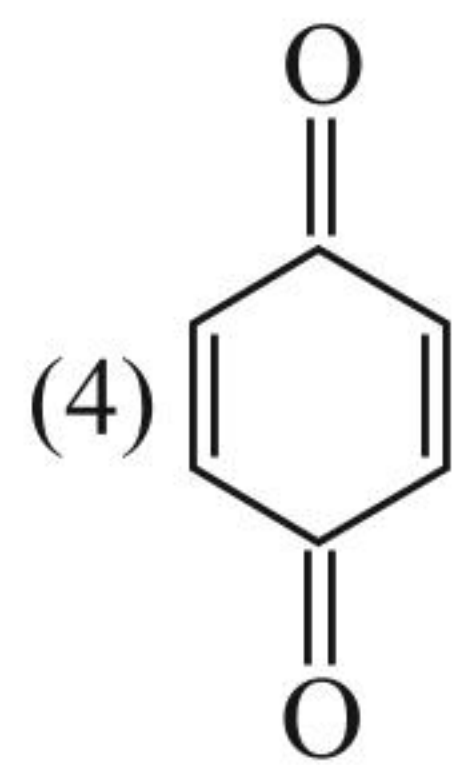
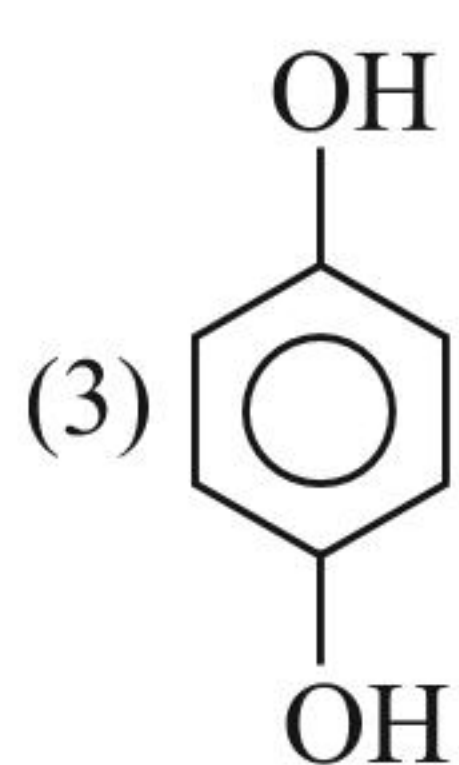
(3)

(4)



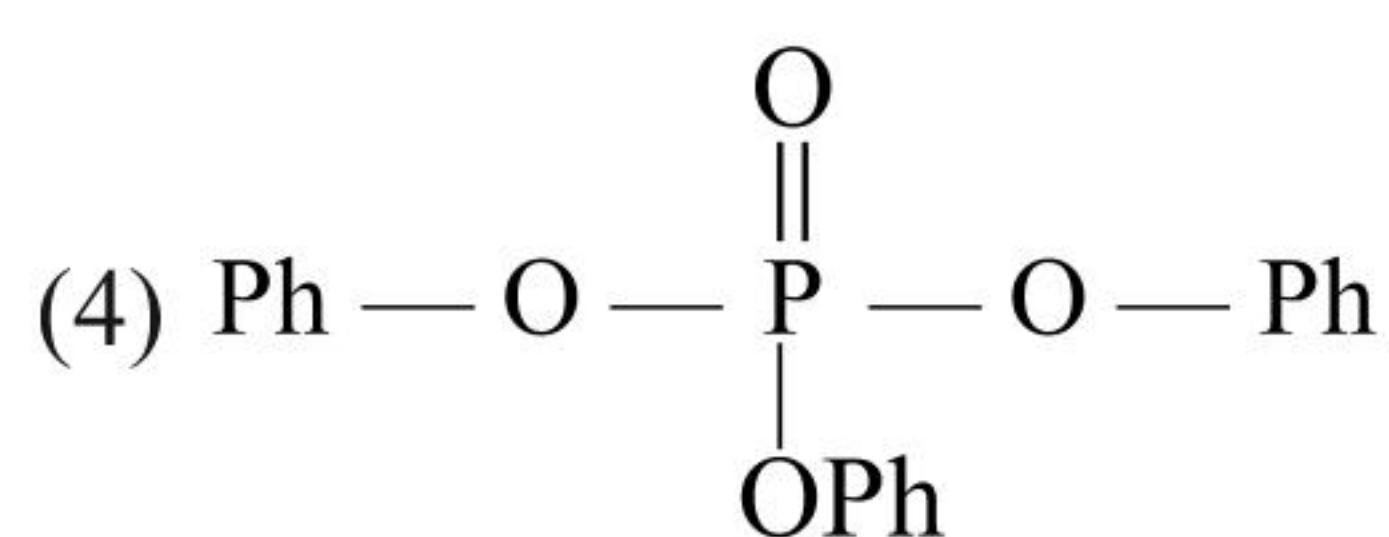
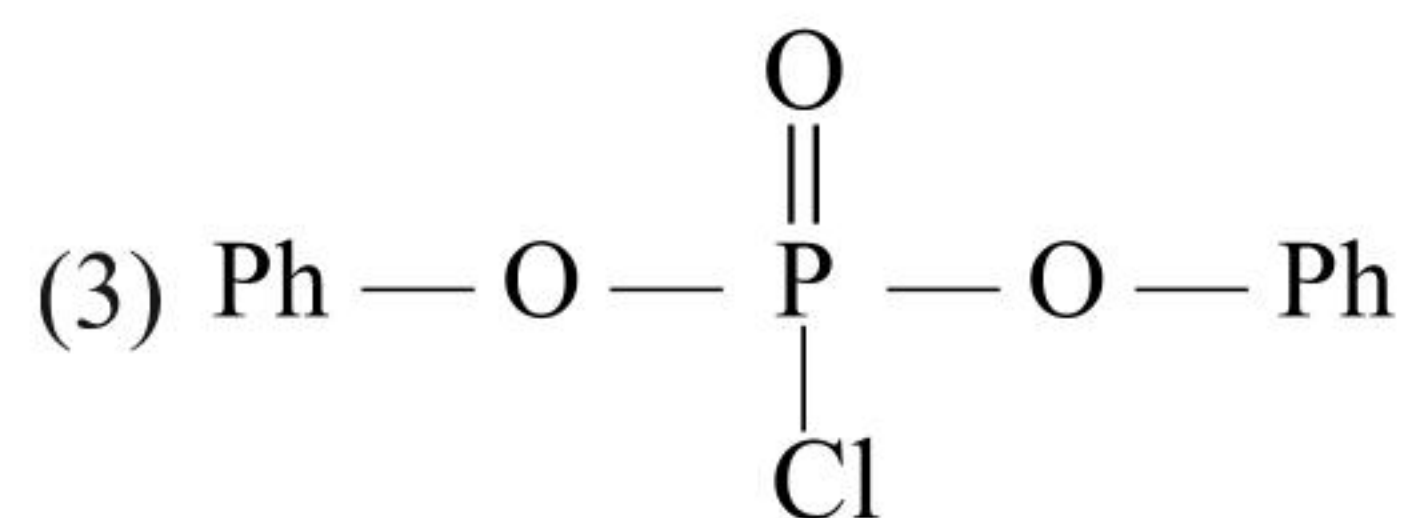
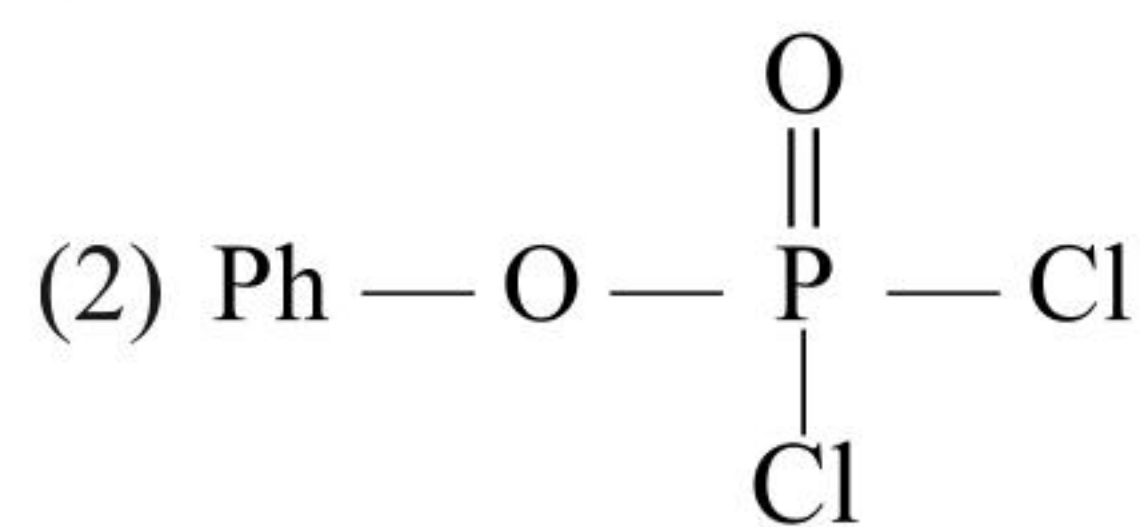
(1)

(2)

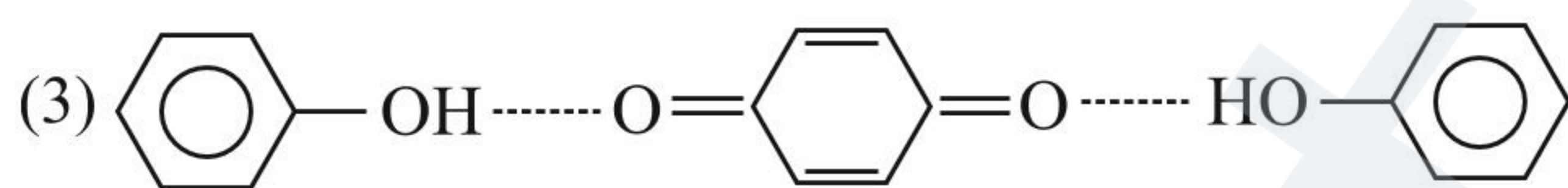
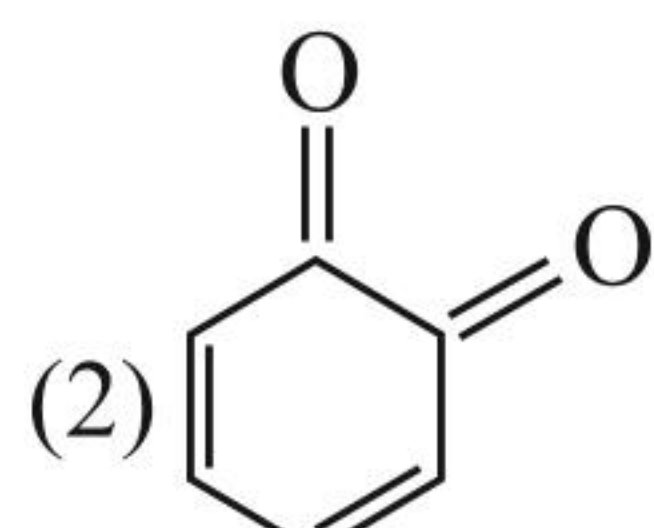
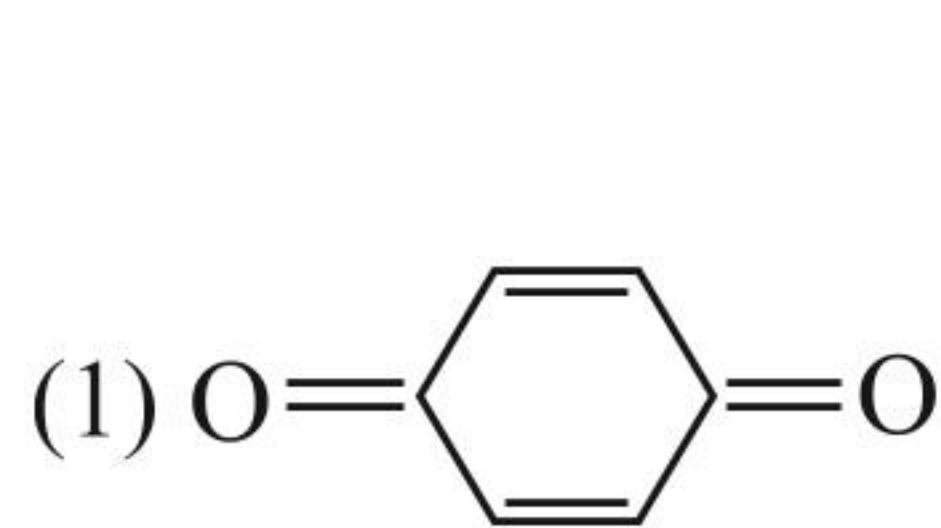


9. Phenol reacts with PCl_5 , the main product is:

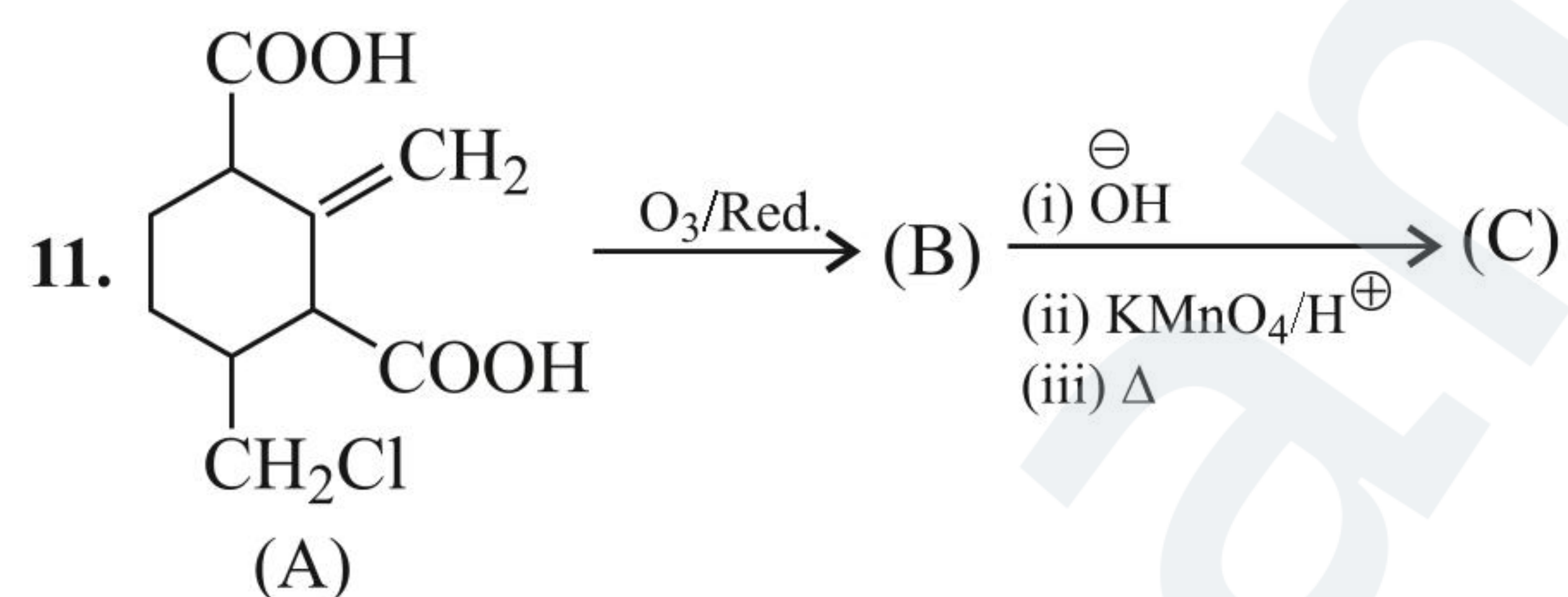
(1) PhCl



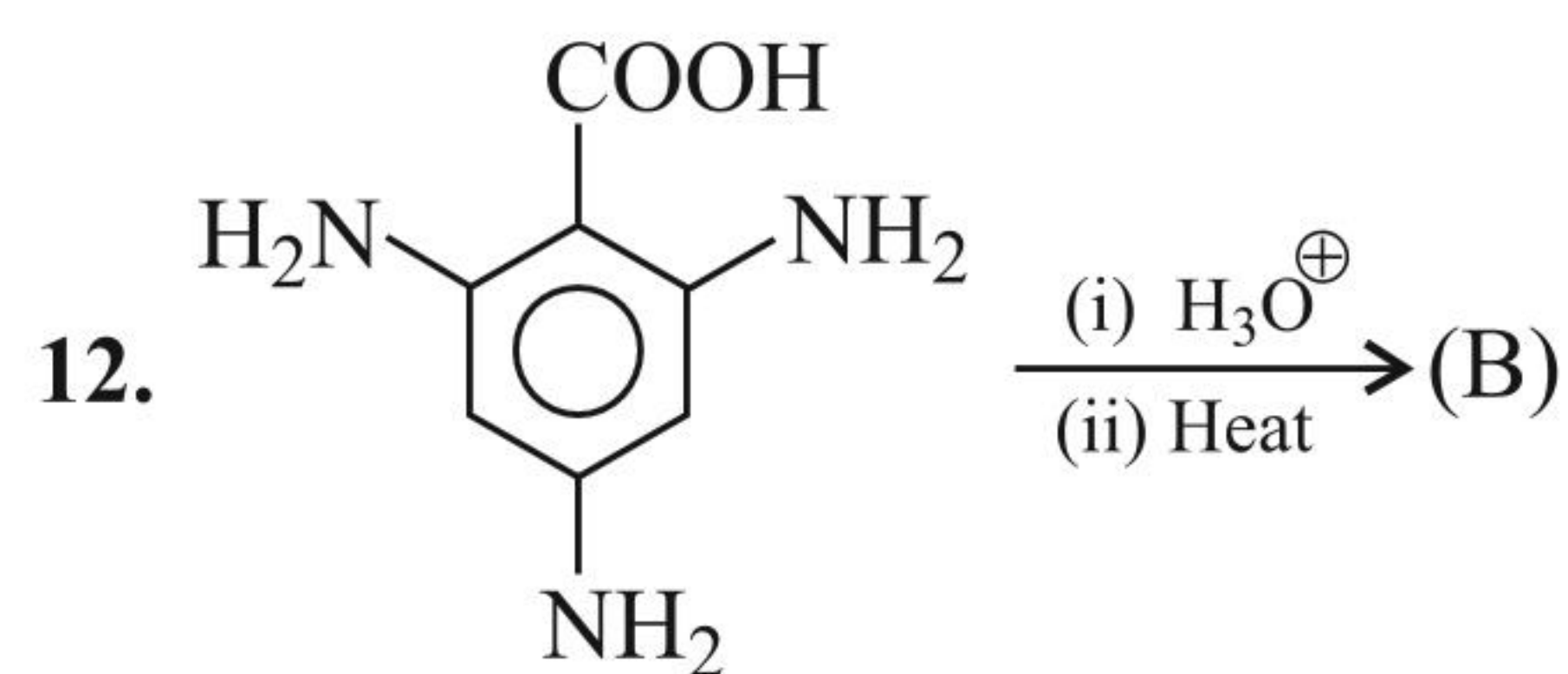
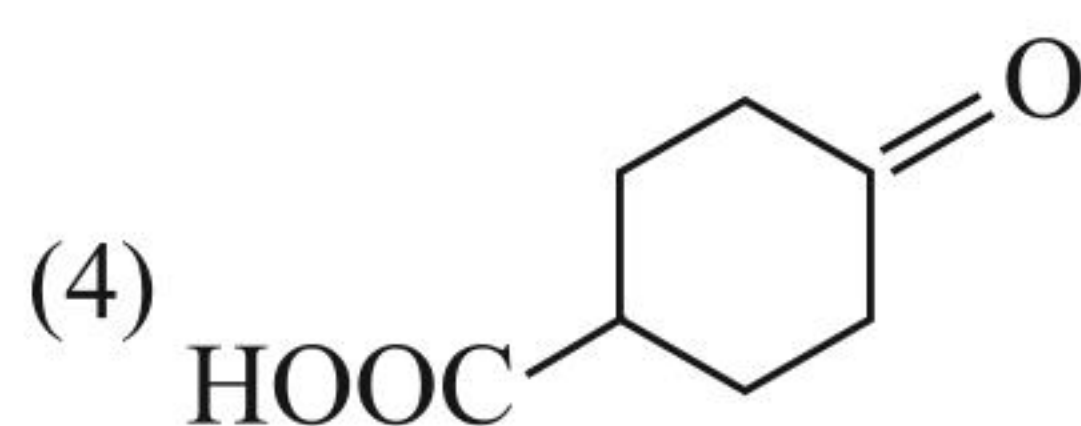
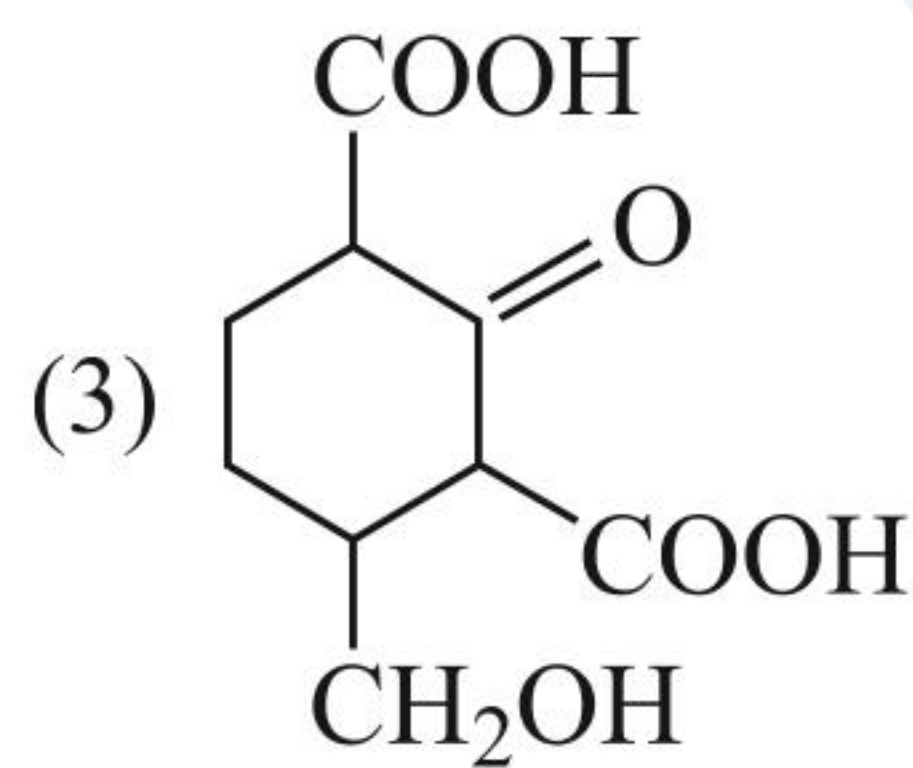
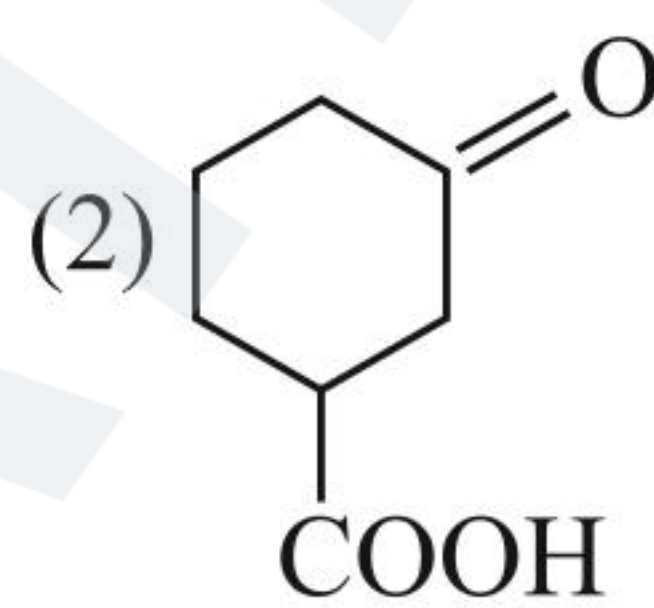
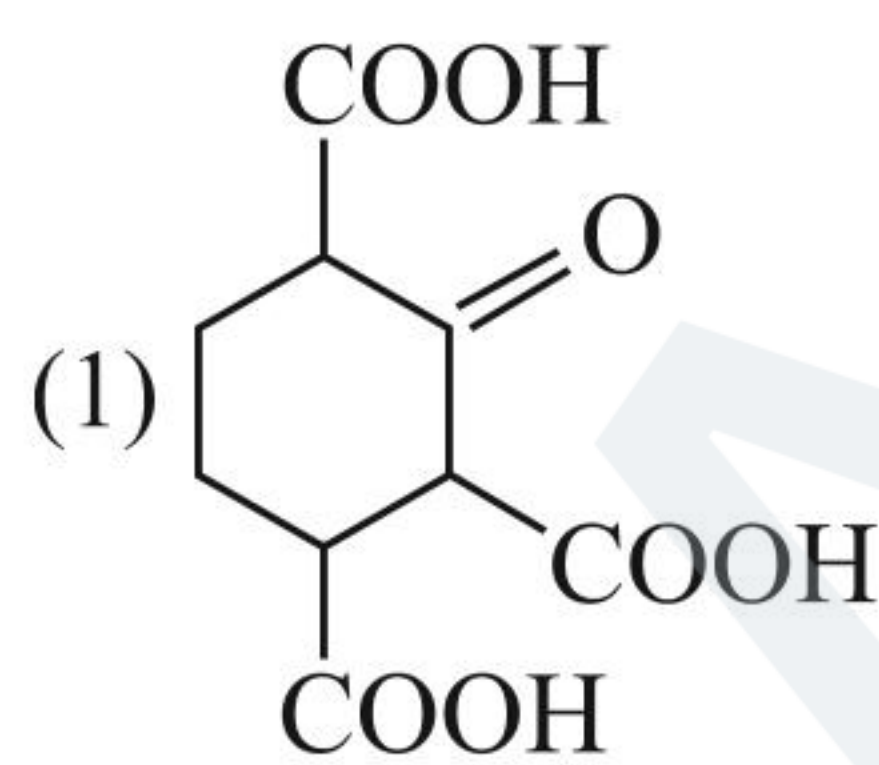
10. Phenol $\xrightarrow[\text{oxid.}]{\text{Aerial}}$ coloured product. This is due to the formation of:



(4) All

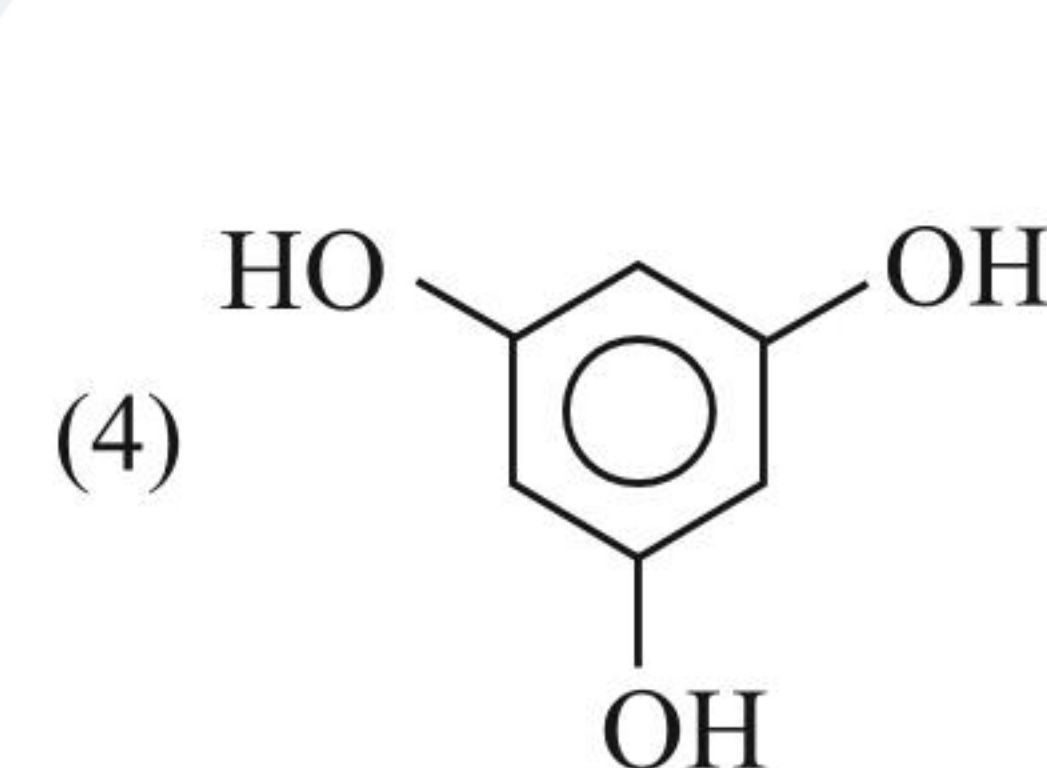
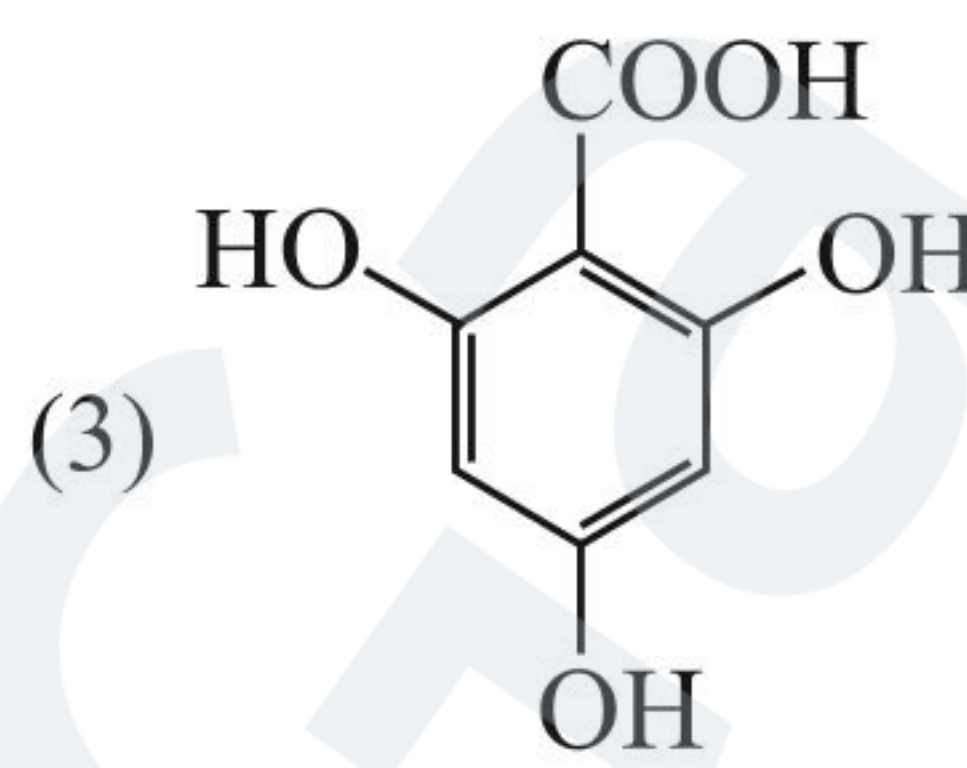
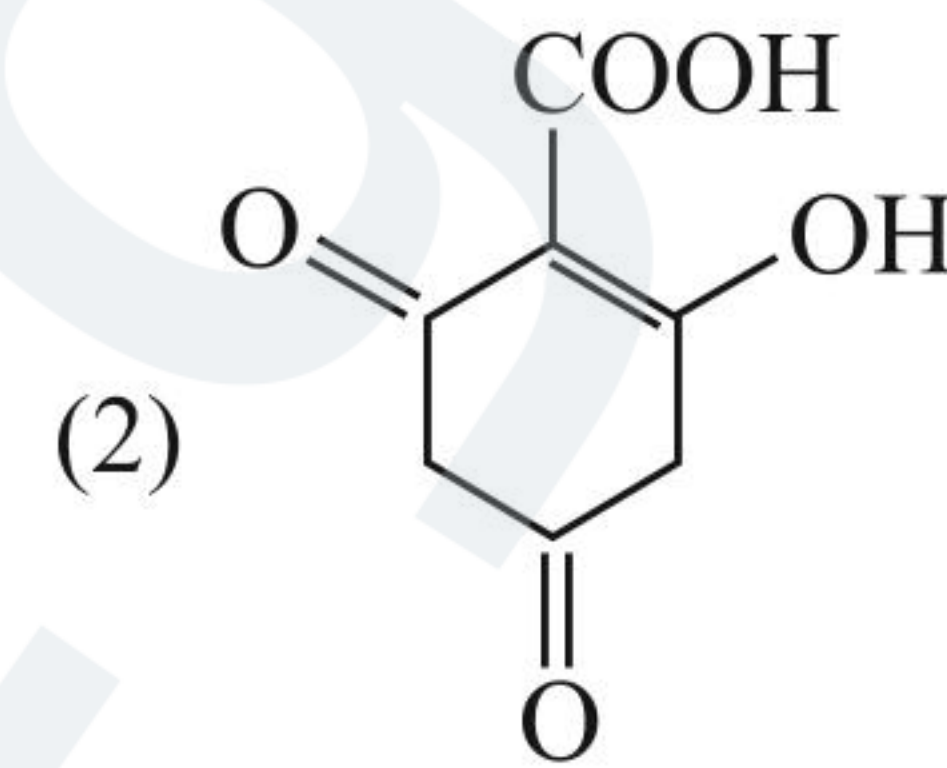
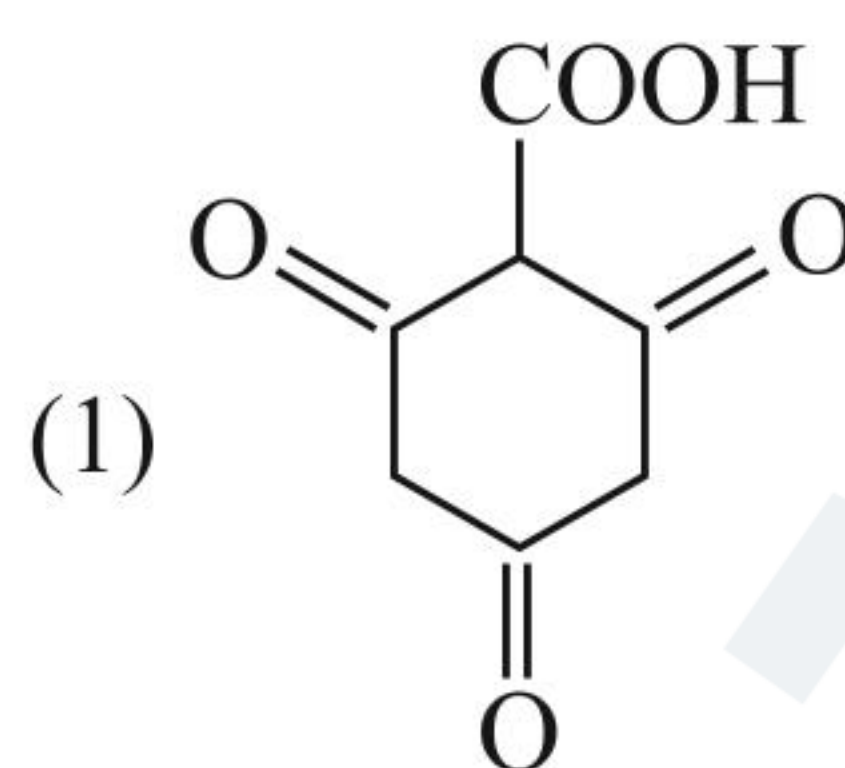


The compound (C) is:

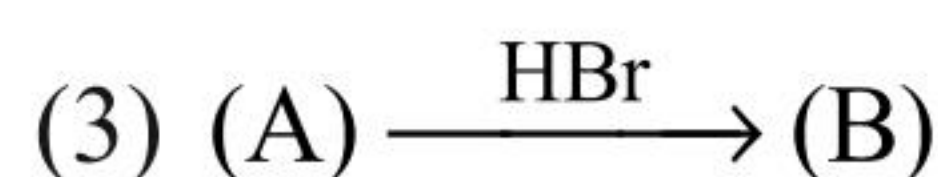
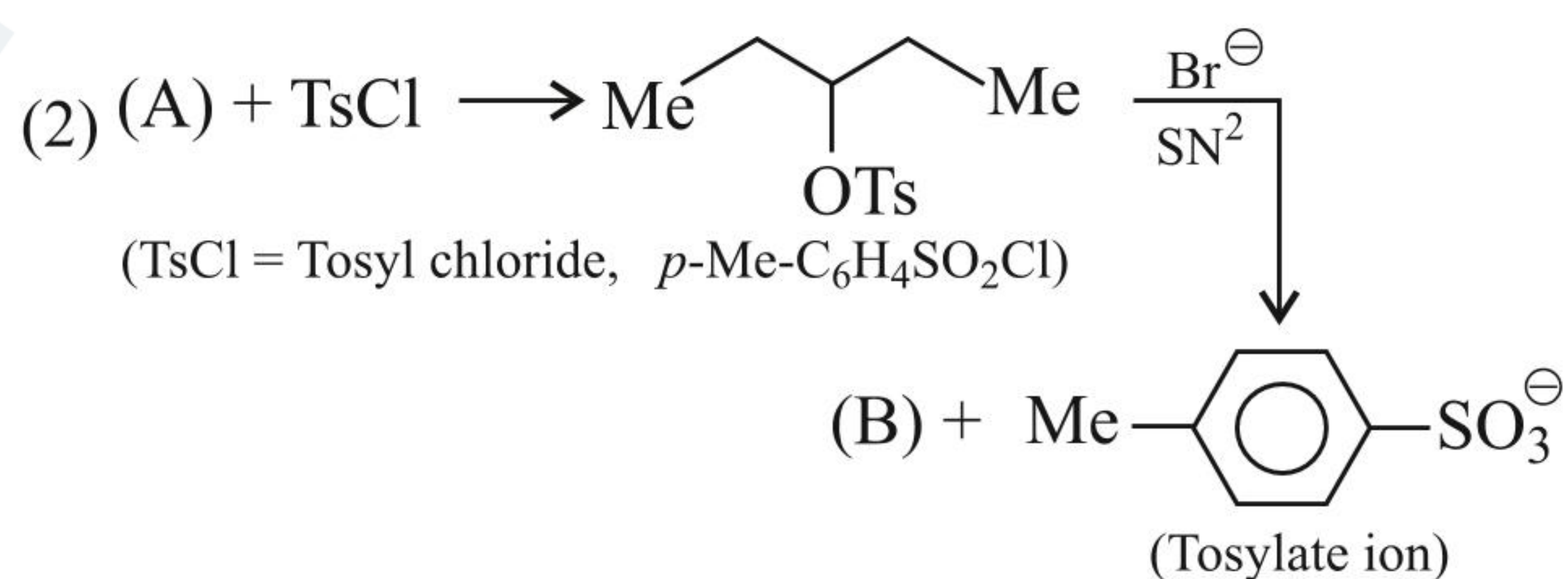
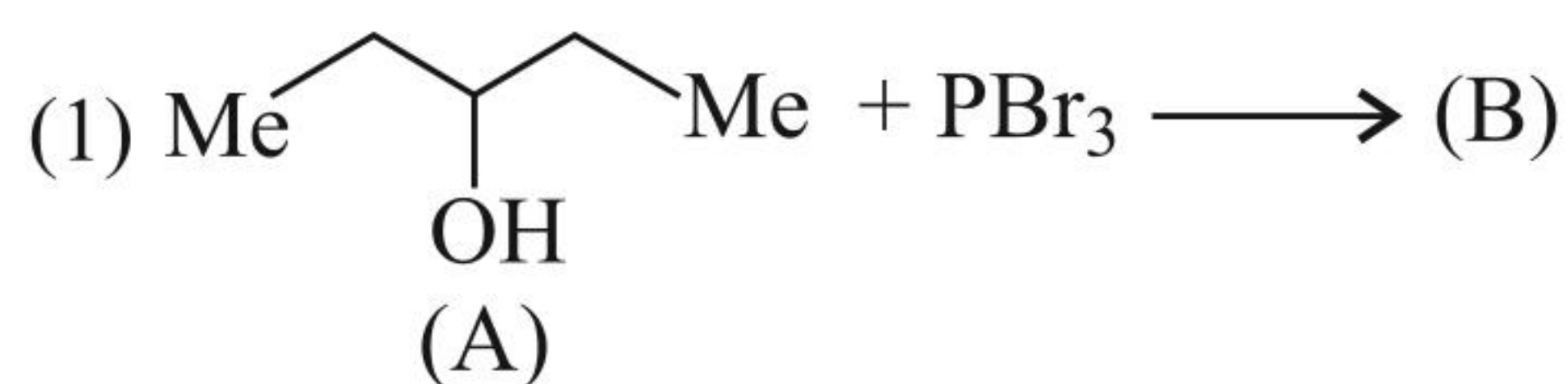


(A)

The product (B) is:



13. Which is the best method for the conversion of (A) pentan-3-ol to 3-bromopentane (B)?



(4) Both (1) and (2)

14. Which statement is correct for the conversion of ROH to RX by reagents (A) (SOCl_2 , PBr_3 , PCl_3 , PI_3 , and TsCl) compared to using HX?

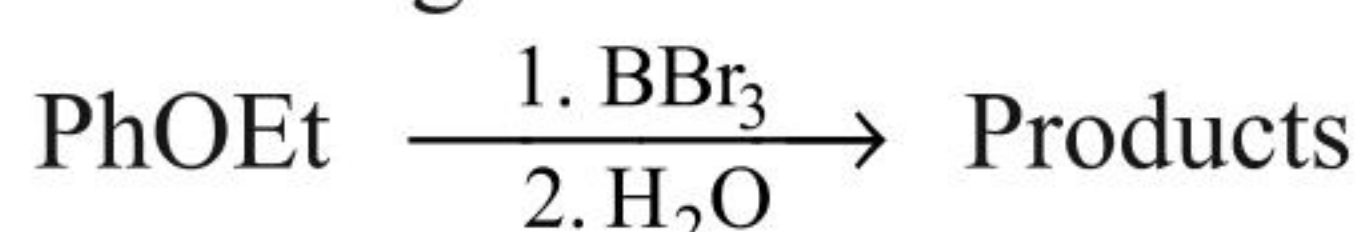
(1) No rearrangement occurs with predictable stereochemistry by reagents (A)

(2) Reagents (A) are not useful for 3° alcohols, while HX reacts easily with 3° alcohols involving no rearrangement.

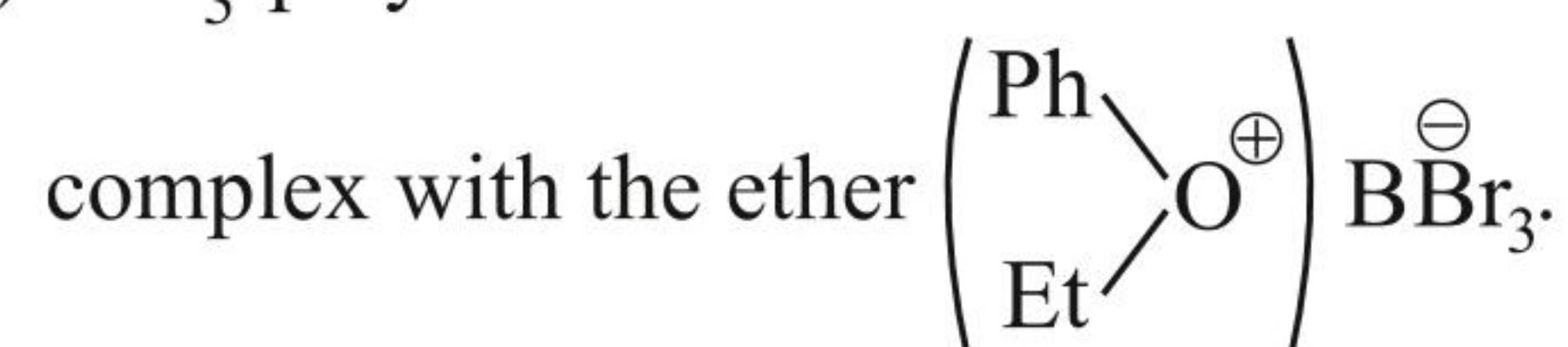
(3) Reagents (A) must be used in anhydrous conditions because all react vigorously with H_2O and they produce harmful gases (SO_2 , HCl , HBr , and HI).

(4) All.

15. Which of the following statements is wrong about the following reaction?

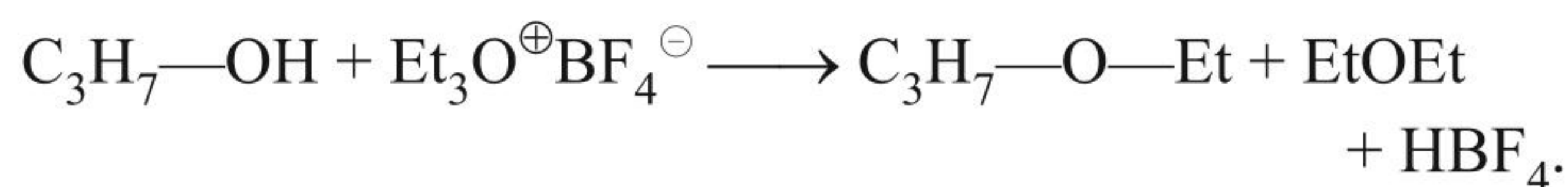


(1) BBr_3 plays a role similar to the H in HI by forming a



- (2) The liberated Br^- attacks Et, displacing PhOBr_2 , which is ultimately hydrolysed to give the products.
 (3) The products are $\text{PhOH} + \text{EtBr} + \text{H}_3\text{BO}_3$.
 (4) The products are $\text{PhBr} + \text{EtOH} + \text{H}_3\text{BO}_3$.

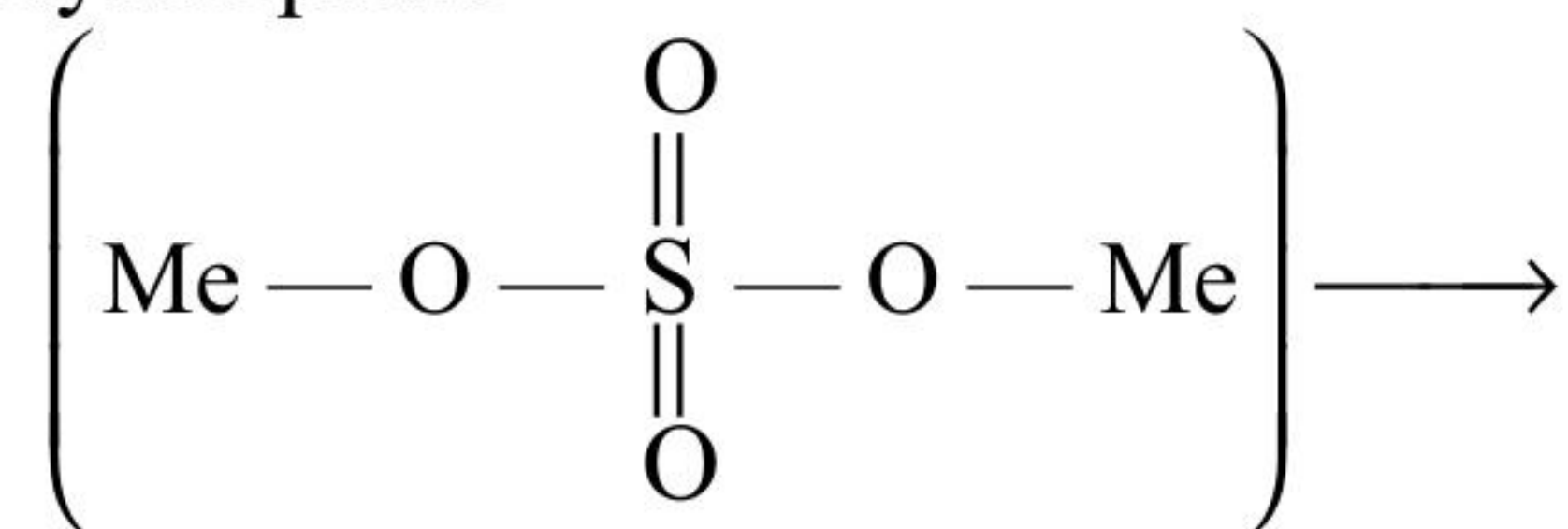
16. Consider the reaction



Which of the following statements is **wrong**?

- (1) The nucleophile in the reaction is $\text{C}_3\text{H}_7\text{OH}$.
 (2) The nucleophile in the reaction is BF_4^- .
 (3) The leaving group is Et_2O .
 (4) $\text{S}_\text{N}2$ reaction occurs.

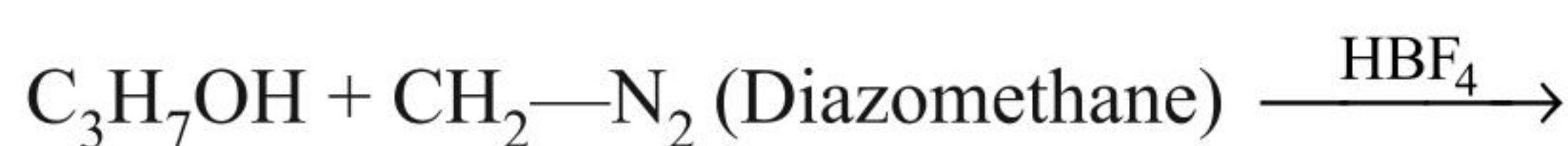
17. Consider the reaction:



The leaving group is:

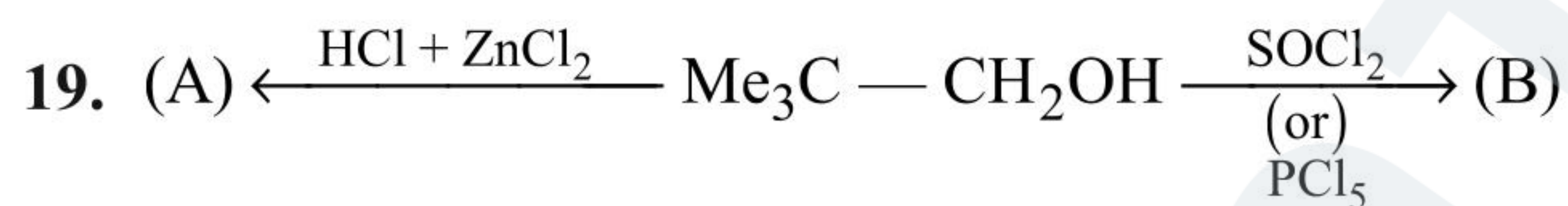
- (1) MeOSO_2O^- (2) MeO^-
 (3) Me^- (4) MeOSO_2^-

18. Consider the reaction



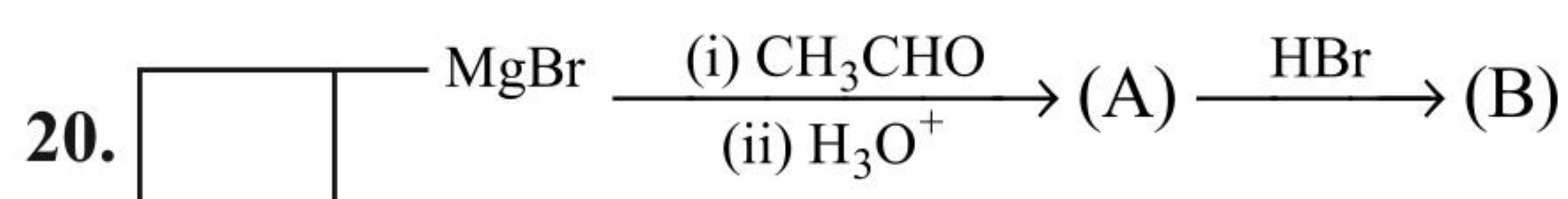
The leaving group is:

- (1) CH_2^- (2) N_2
 (3) BF_4^- (4) $\text{C}_3\text{H}_7\text{O}^-$



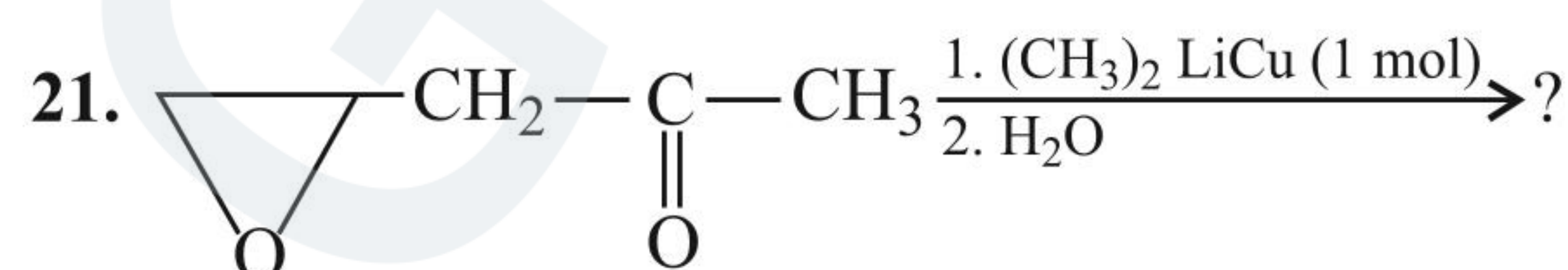
(A) and (B) are:

- | A | B |
|--|---|
| (1) $\text{Me}_3\text{C—CH}_2\text{Cl}$ | $\text{Me}_3\text{C—CH}_2\text{Cl}$ |
| (2) $\text{Me—}\overset{\text{Me}}{\underset{\text{Cl}}{\text{C}}}\text{—CH}_2\text{Me}$ | $\text{Me}_3\text{C—CH}_2\text{Cl}$ |
| (3) $\text{Me}_3\text{C—CH}_2\text{Cl}$ | $\text{Me—}\overset{\text{Me}}{\underset{\text{Cl}}{\text{C}}}\text{—CH}_2\text{—Me}$ |
| (4) $\text{Me—}\overset{\text{Me}}{\underset{\text{Cl}}{\text{C}}}\text{—CH}_2\text{Me}$ | $\text{Me—}\overset{\text{Me}}{\underset{\text{Cl}}{\text{C}}}\text{—CH}_2\text{—Me}$ |



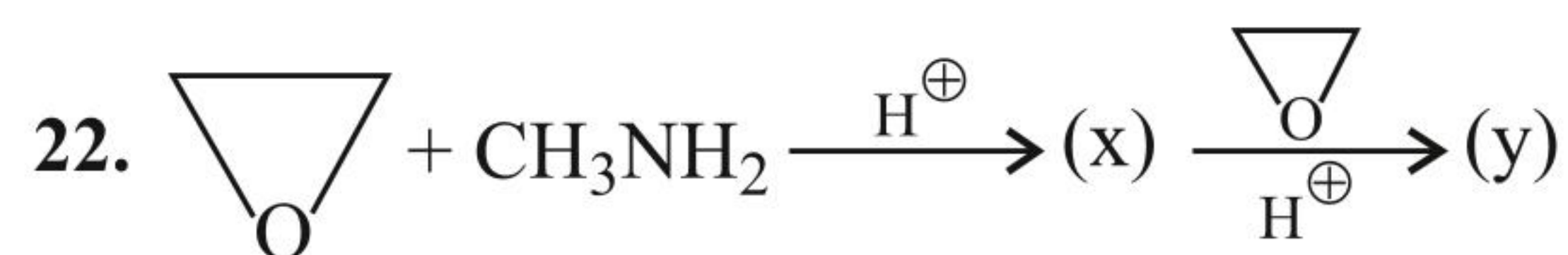
The compounds (A) and (B) are

- | A | B |
|-----|---|
| (1) | |
| (2) | |
| (3) | |
| (4) | |



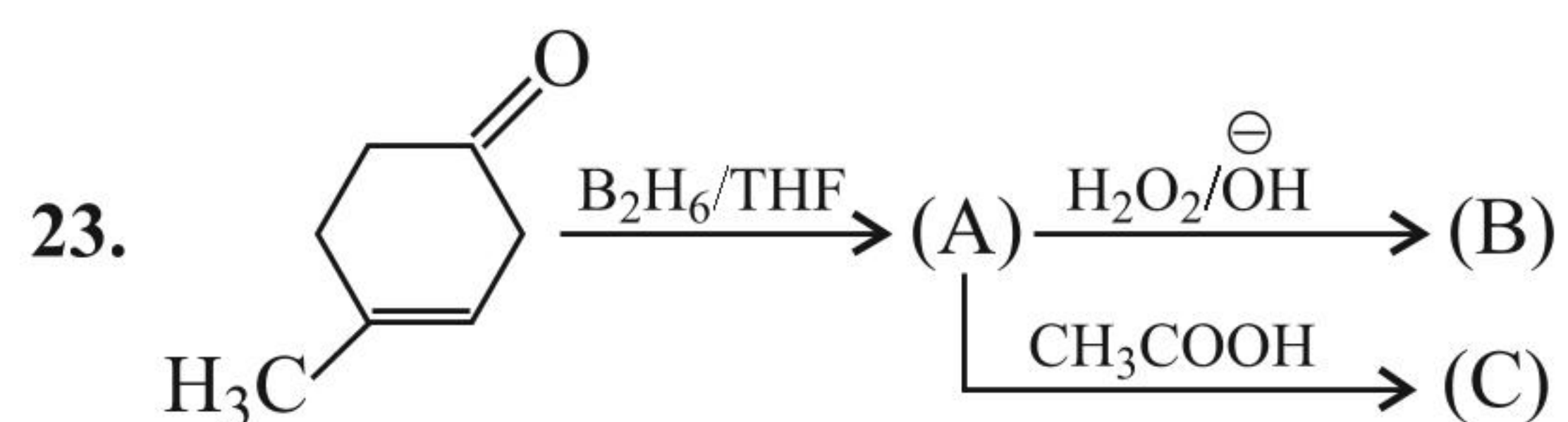
The product is:

- (1) $\text{CH}_3\text{—CH}_2\text{—}\underset{\text{OH}}{\text{CH}}\text{—CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$
 (2) $\text{CH}_3\text{—CH}_2\text{—}\underset{\text{OH}}{\text{CH}}\text{—CH}_2\text{—}\overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}}\text{—CH}_3$
 (3) (4) All

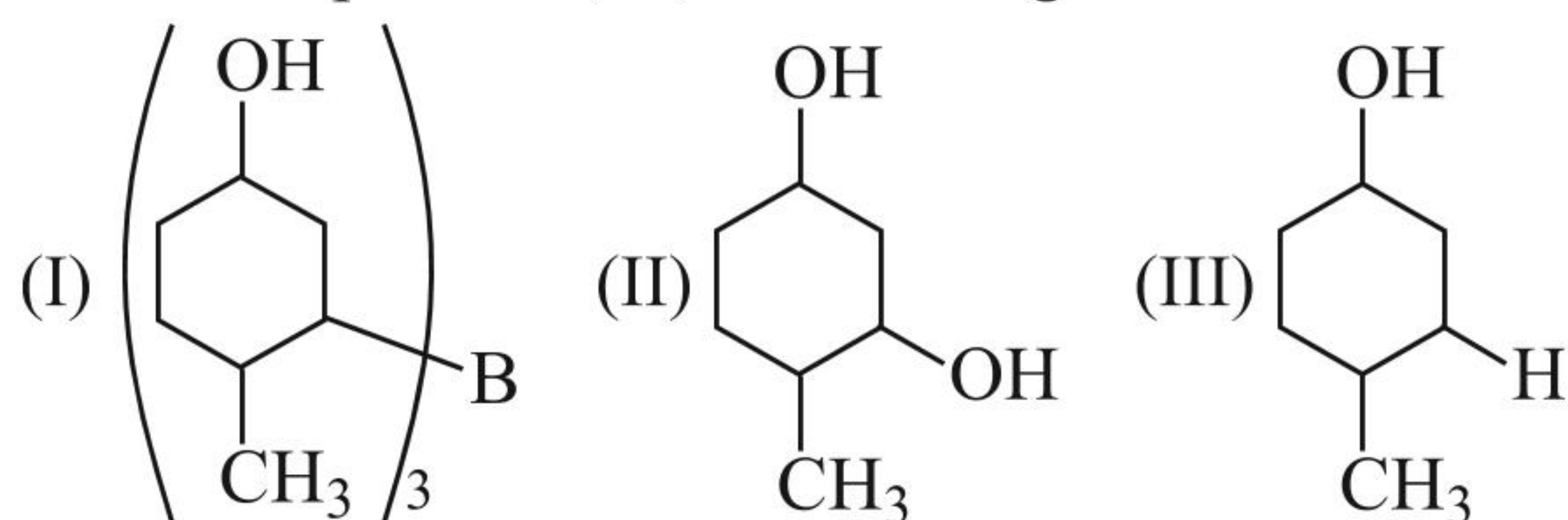


The products (x) and (y) are:

- (1) $\text{x} = \text{HOCH}_2\text{—CH}_2\text{—NH—CH}_3$
 $\text{y} = \text{HOH}_2\text{C—CH}_2\text{—}\underset{\text{CH}_3}{\text{N}}\text{—CH}_2\text{CH}_2\text{OH}$
 (2) $\text{x} = \text{HOCH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$
 $\text{y} = \text{HOH}_2\text{C—CH}_2\text{—CH}_2\text{—NH—CH}_2\text{—CH}_2\text{OH}$
 (3) $\text{x} = \text{HOCH}_2\text{—CH}_2\text{—NH—CH}_3$
 $\text{y} = \text{HOCH}_2\text{—CH}_2\text{—CH}_2\text{—NH—CH}_2\text{—CH}_2\text{OH}$
 (4) $\text{x} = \text{HO—CH}_2\text{—CH}_2\text{—CH}_2\text{NH}_2$
 $\text{y} = \text{HO—CH}_2\text{—CH}_2\text{—}\underset{\text{CH}_3}{\text{N}}\text{—CH}_2\text{CH}_2\text{OH}$

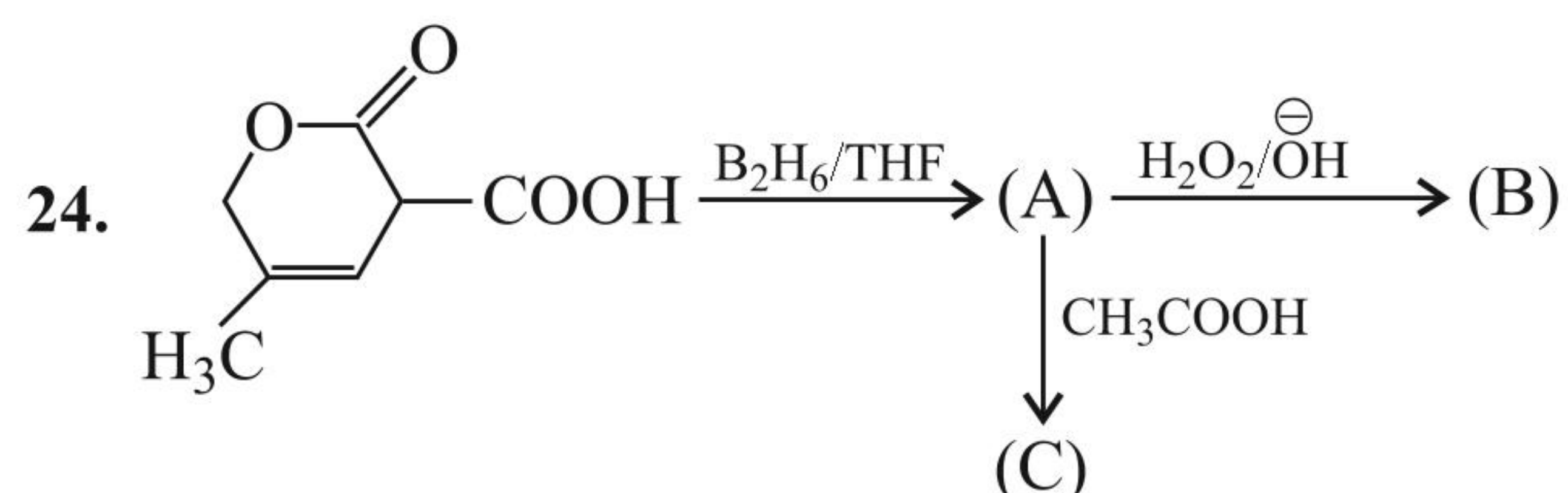


Three compounds I, II, and III are given.

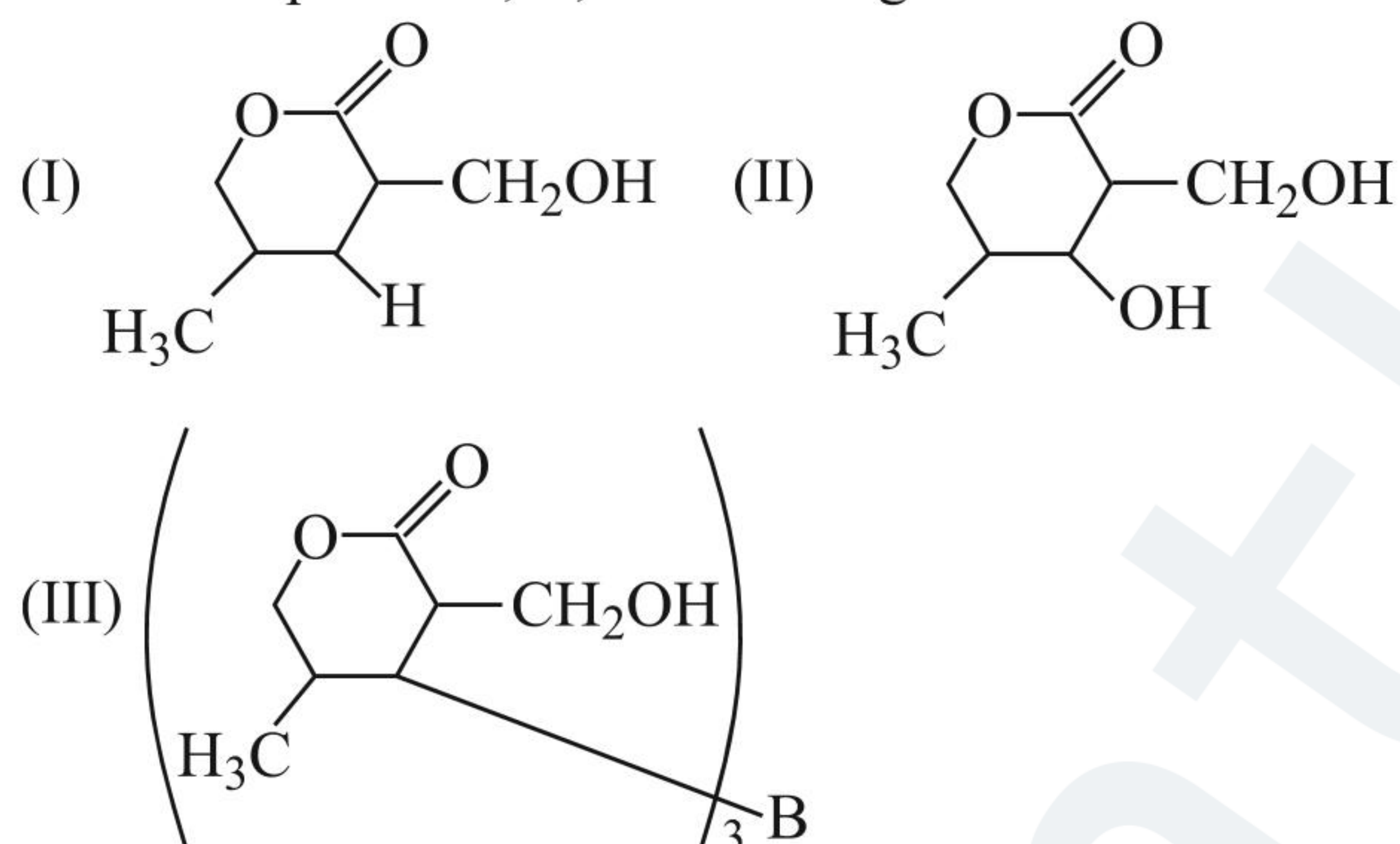


The compounds (A), (B), and (C), respectively, are:

- (1) I, II, and III (2) I, III, and II
(3) II, I, and III (4) II, III, and I.



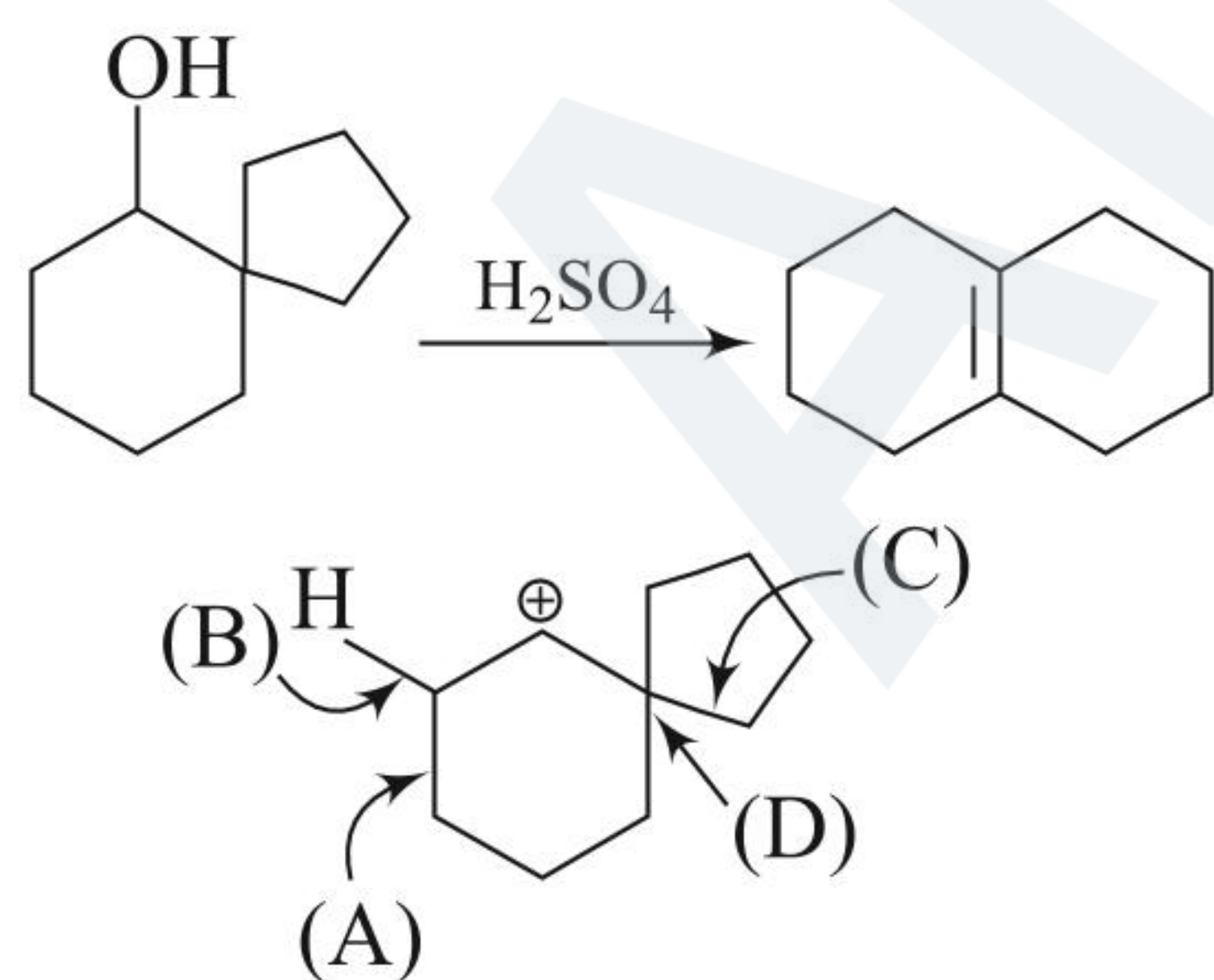
Three compounds I, II, and III are given.



The compounds (A), (B), and (C), respectively, are:

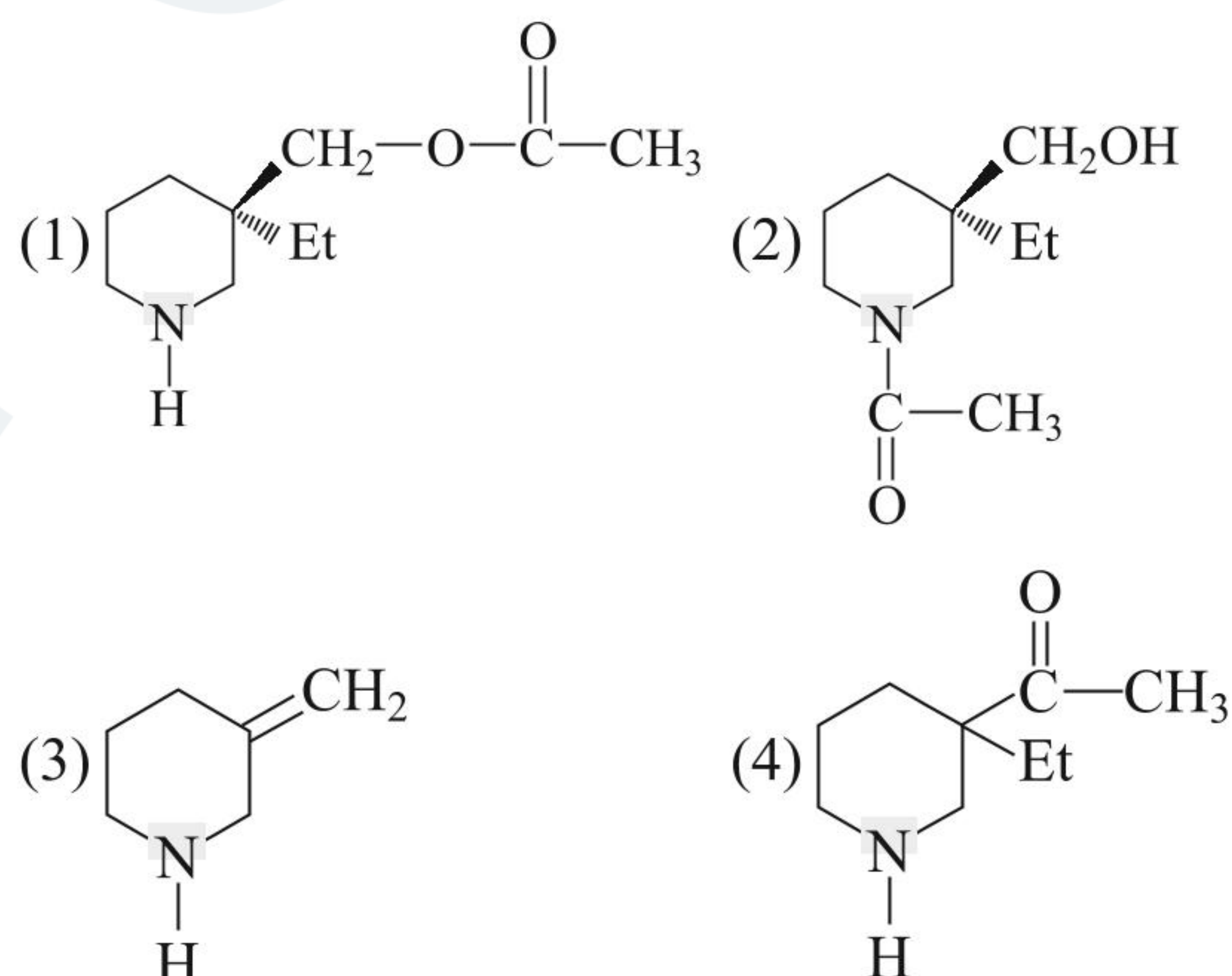
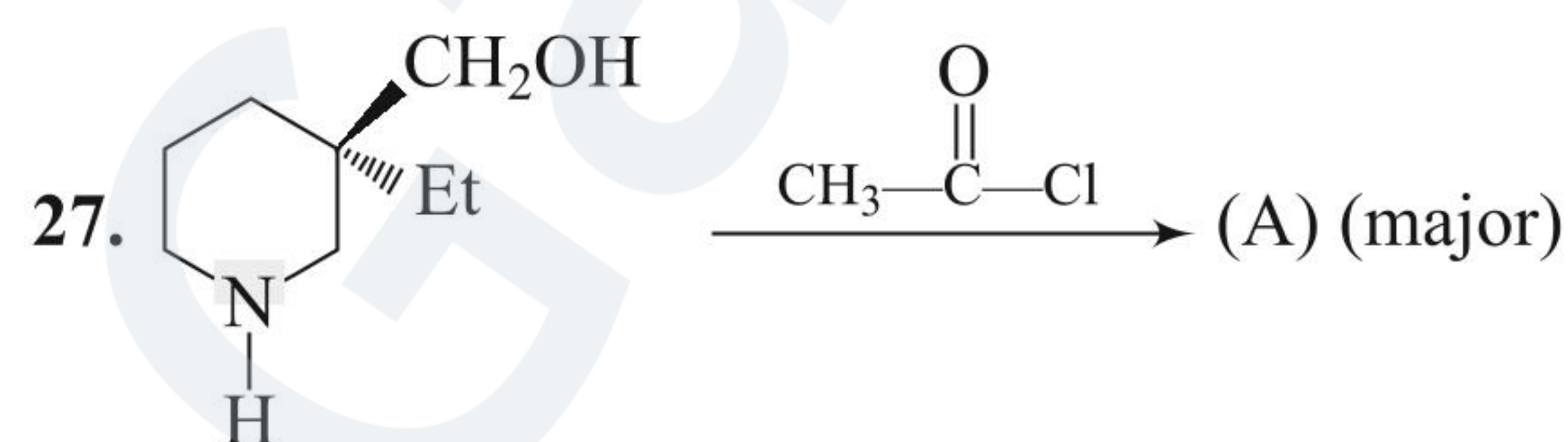
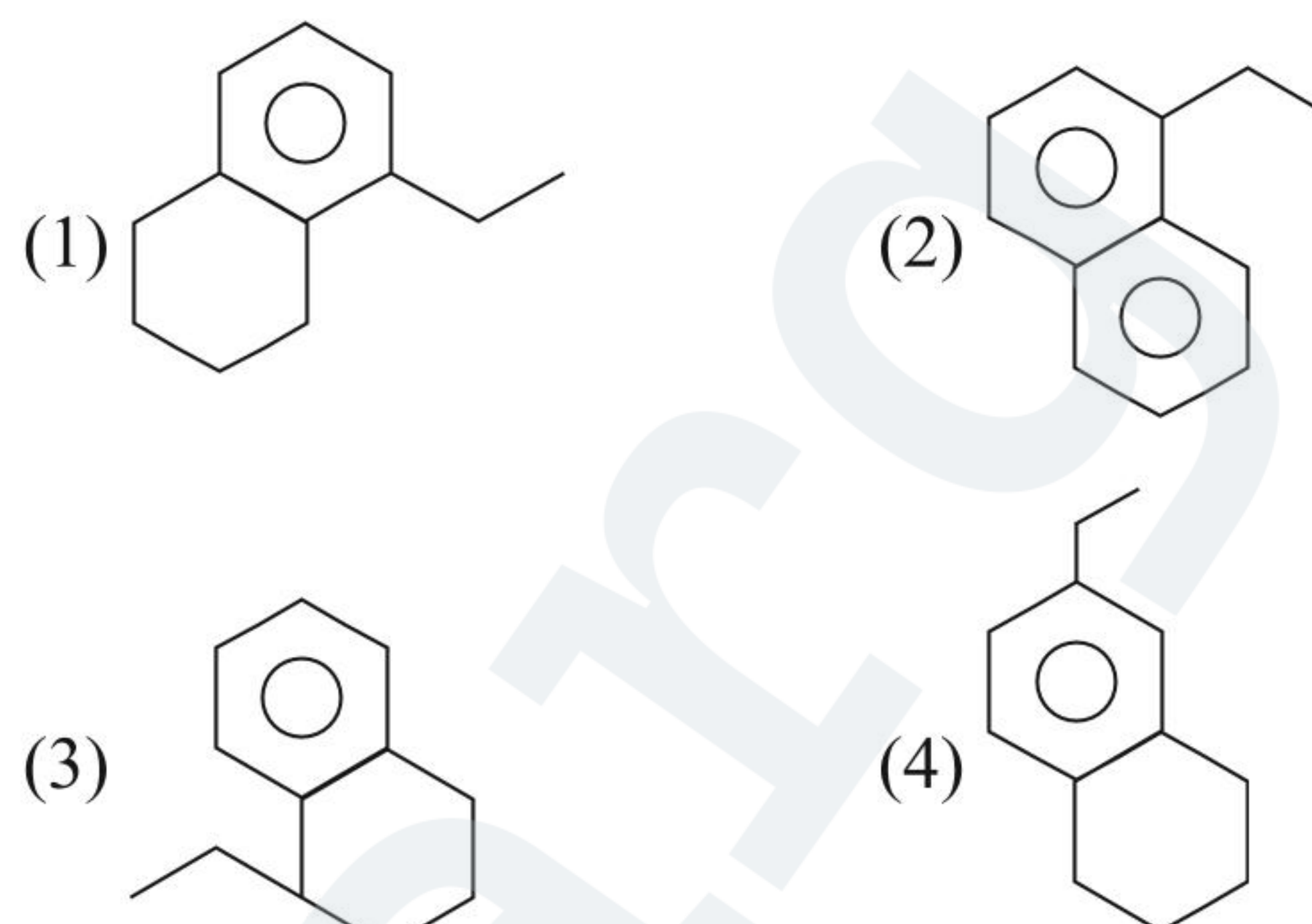
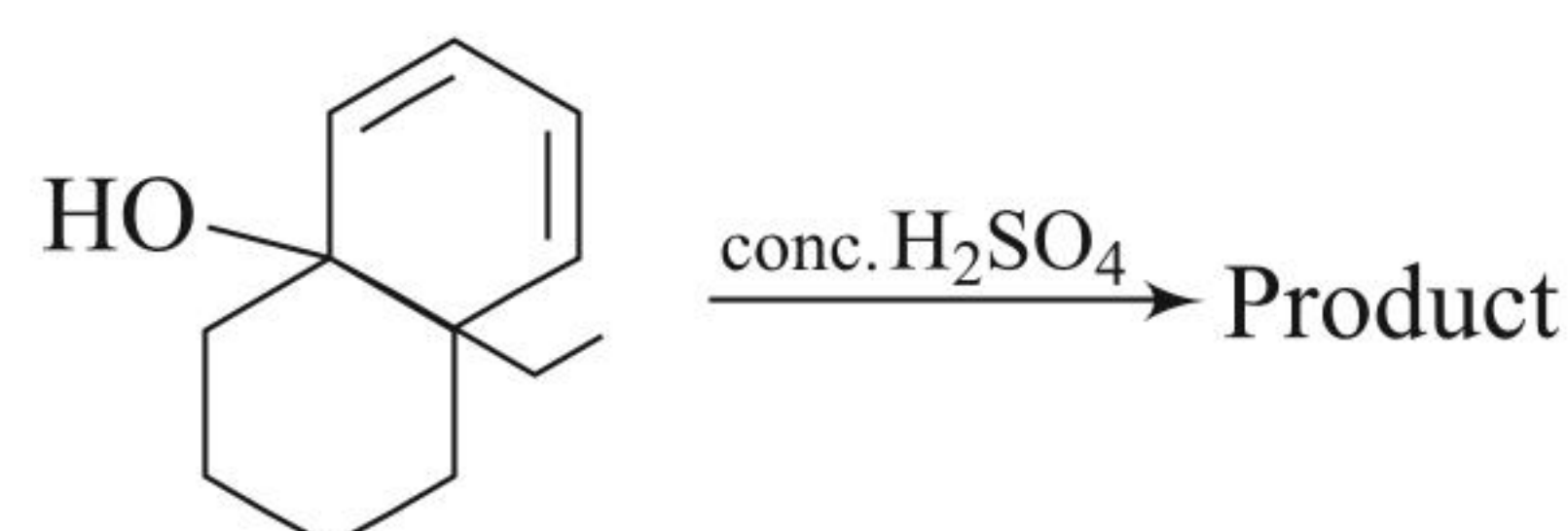
- (1) I, II, and III (2) I, III, and II
(3) III, II, and I (4) III, I, and II

25. The following transformation involves a carbocation rearrangement. The carbocation is generated by protonation of the hydroxyl group, followed by the loss of water. Which bond has to migrate in the carbocation to yield the product indicated (after the deprotonation)?

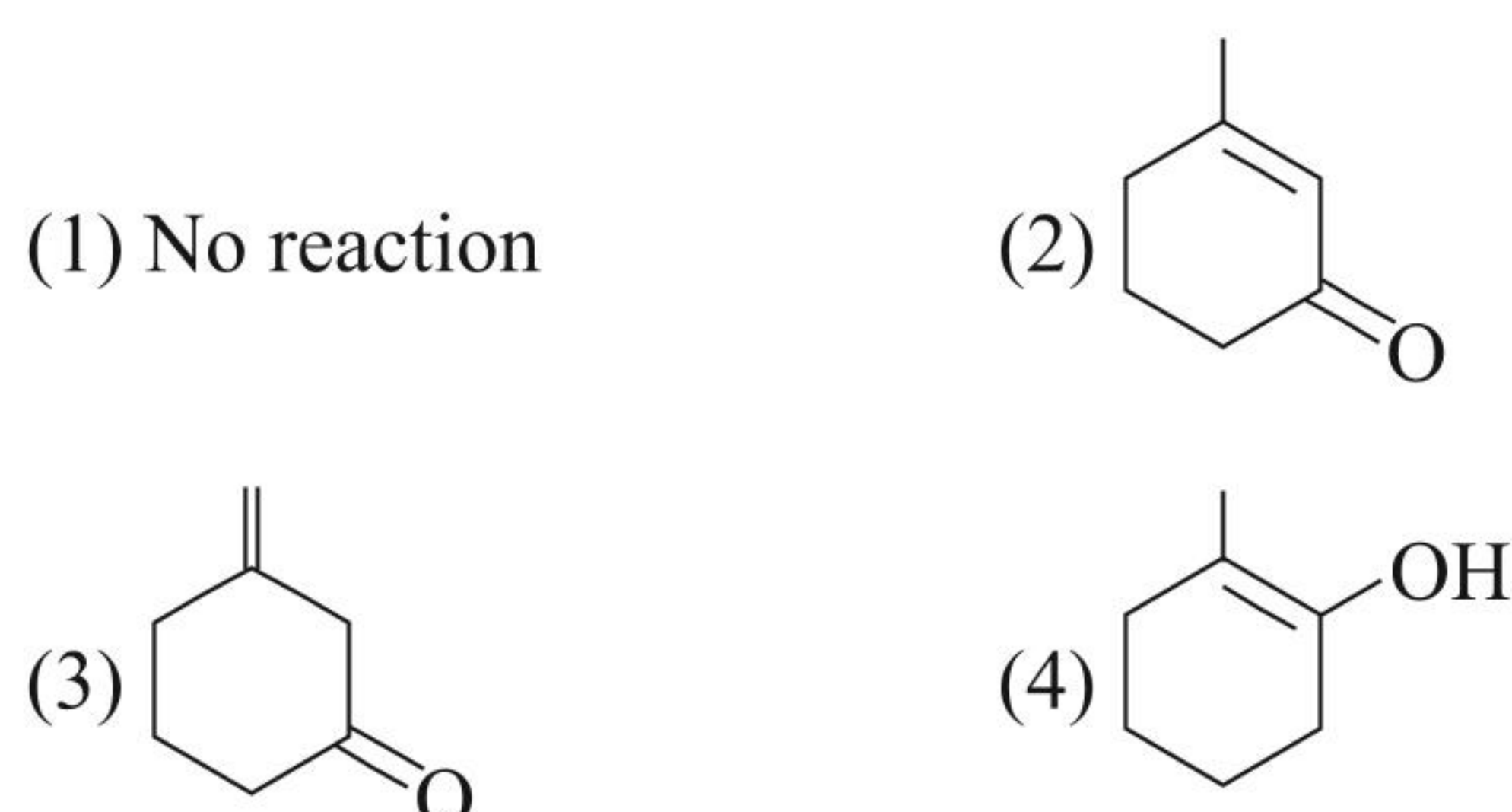
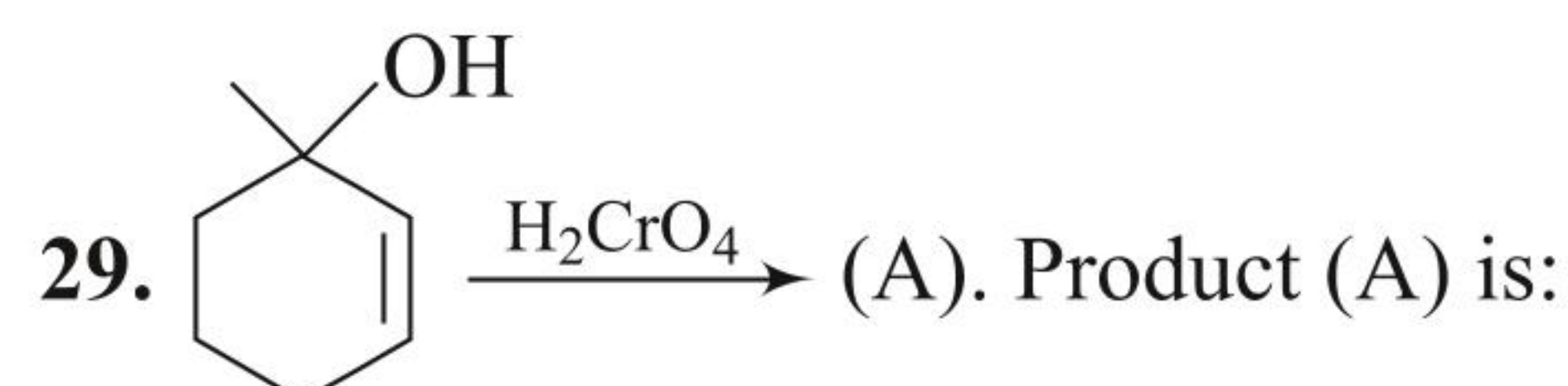
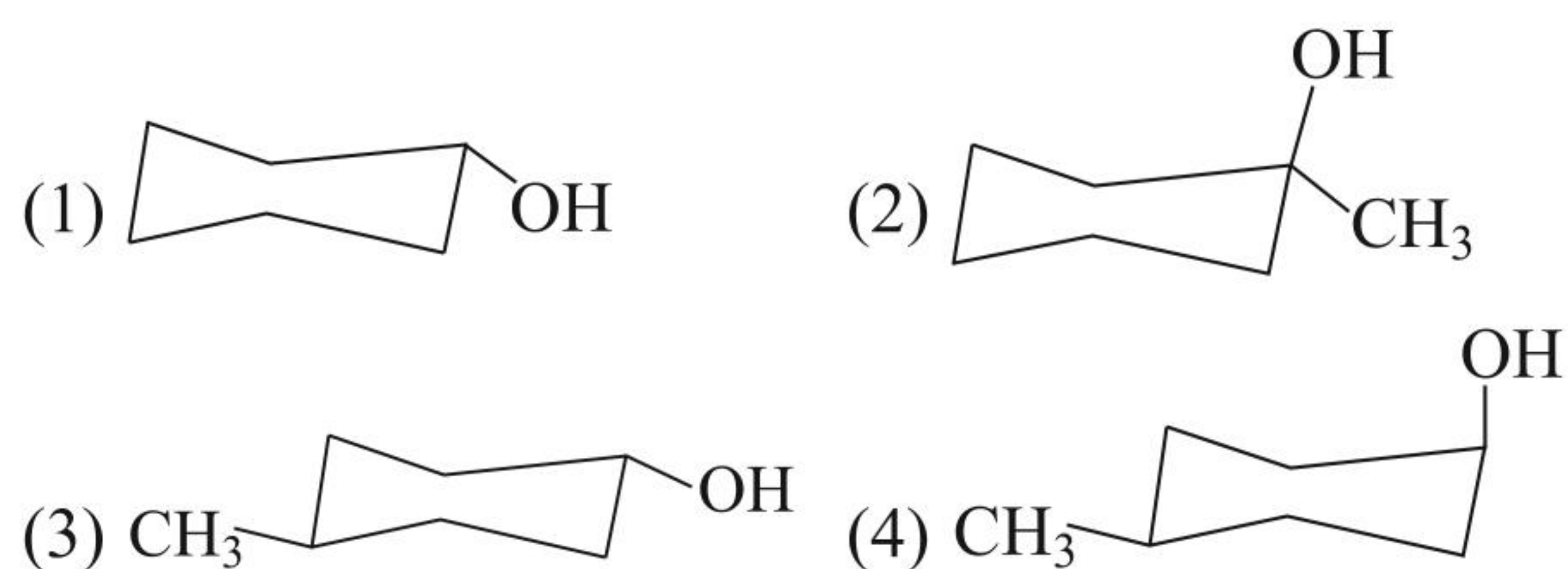


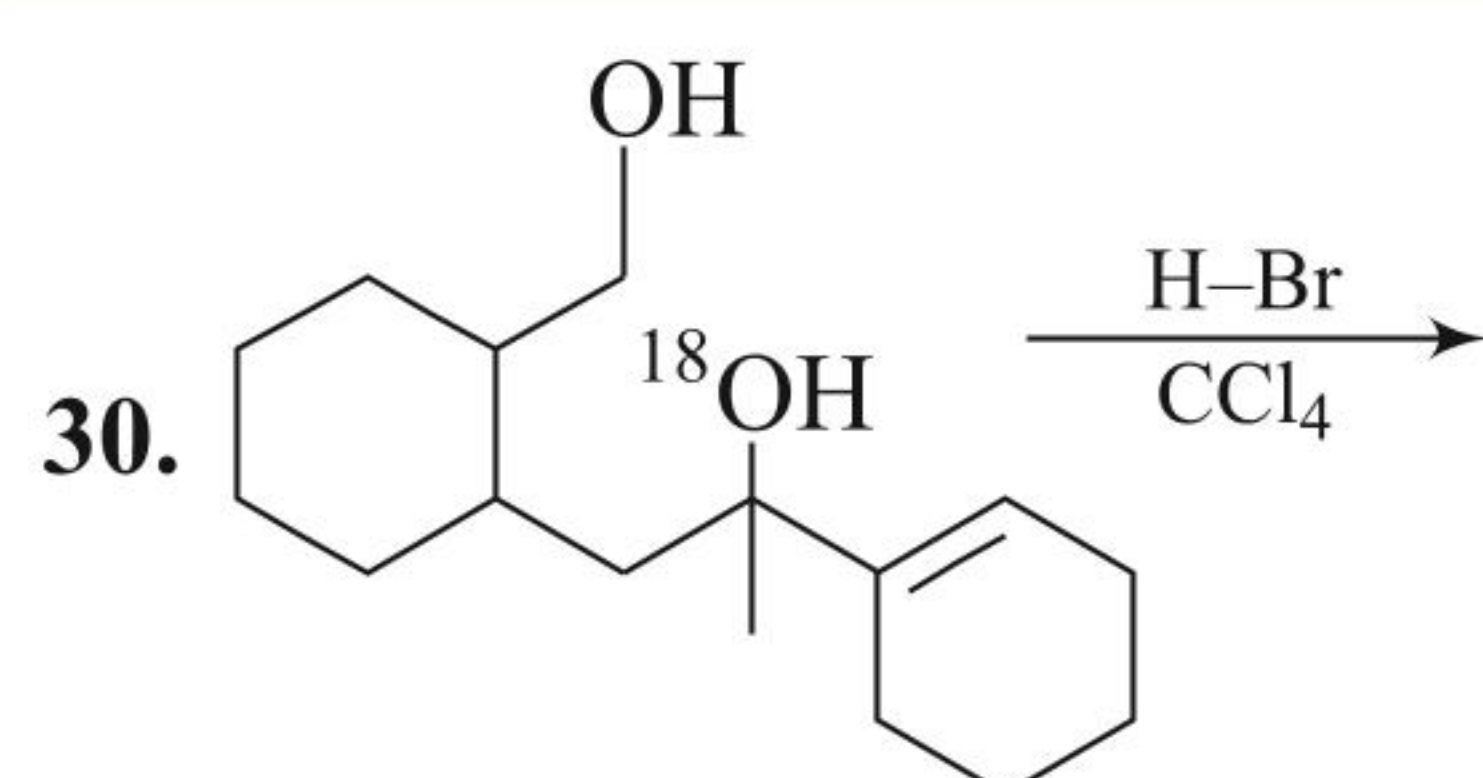
- (1) A (2) B
(3) C (4) D

26. Identify the major product.

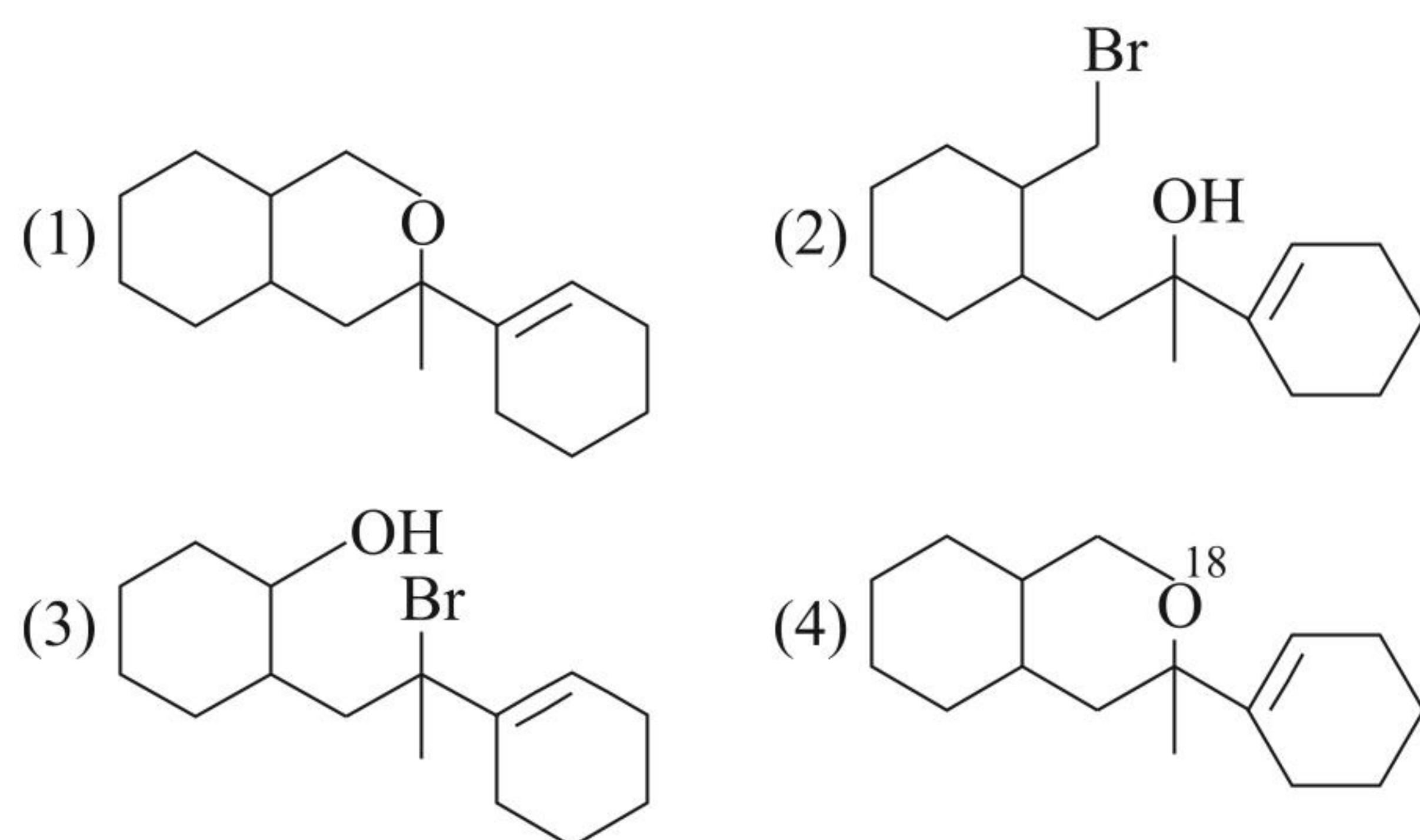


28. Which of the following react with HBr at faster rate?

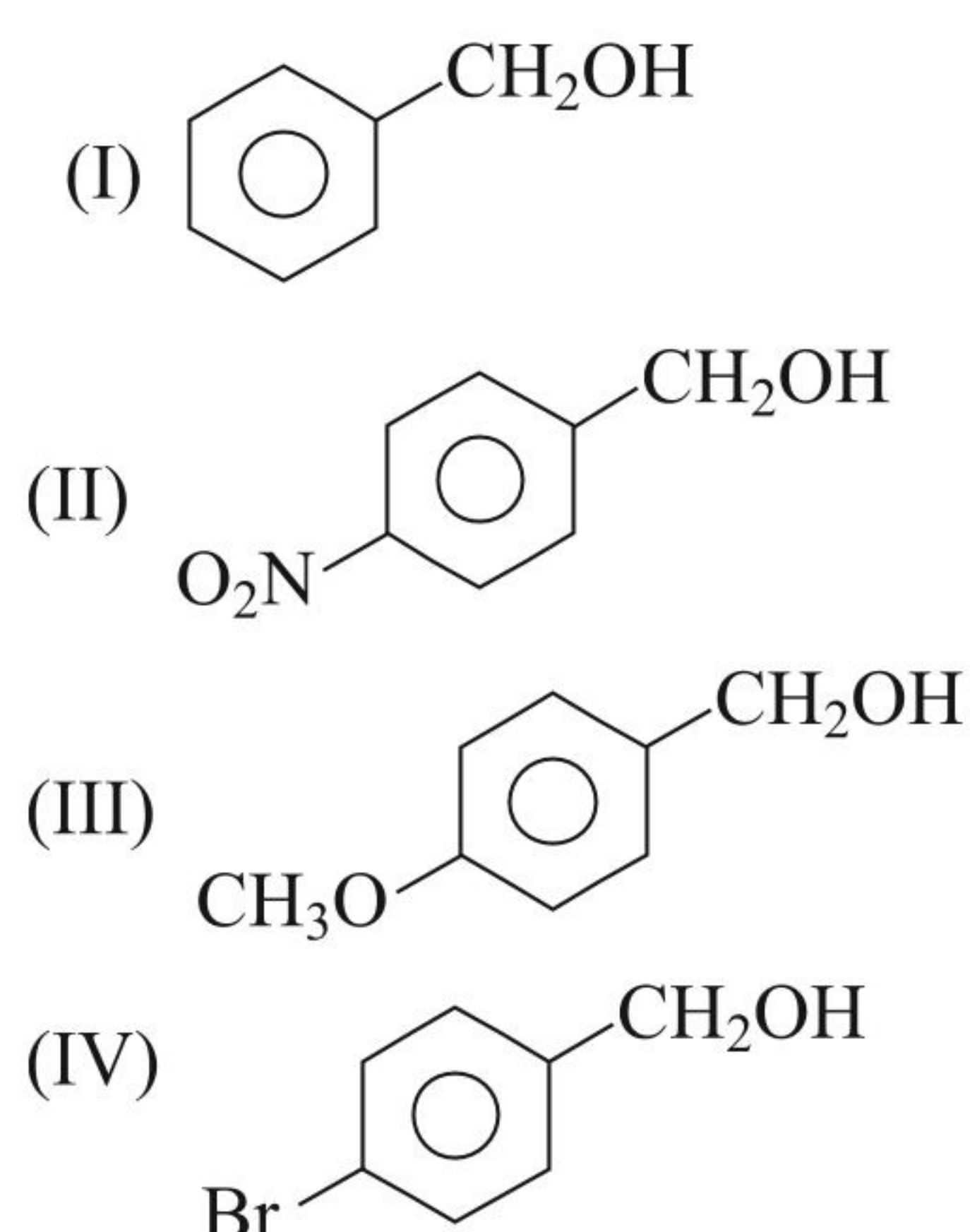




Major product obtained in the reaction is:

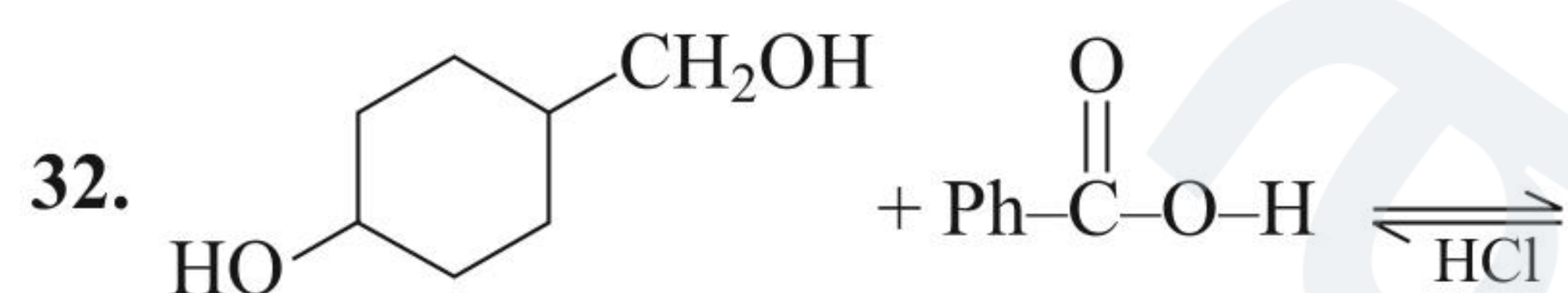


31. Consider the following alcohols,

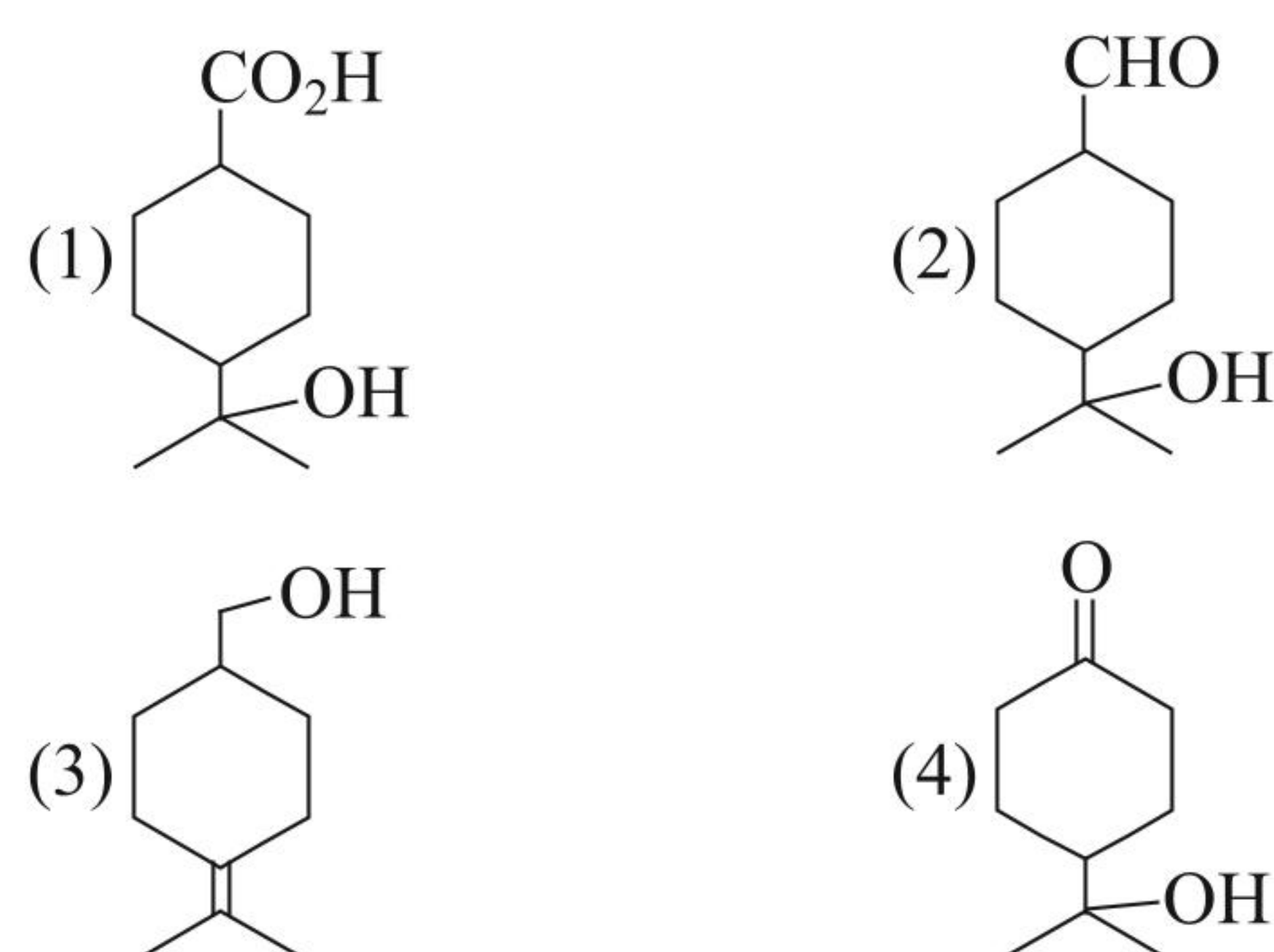
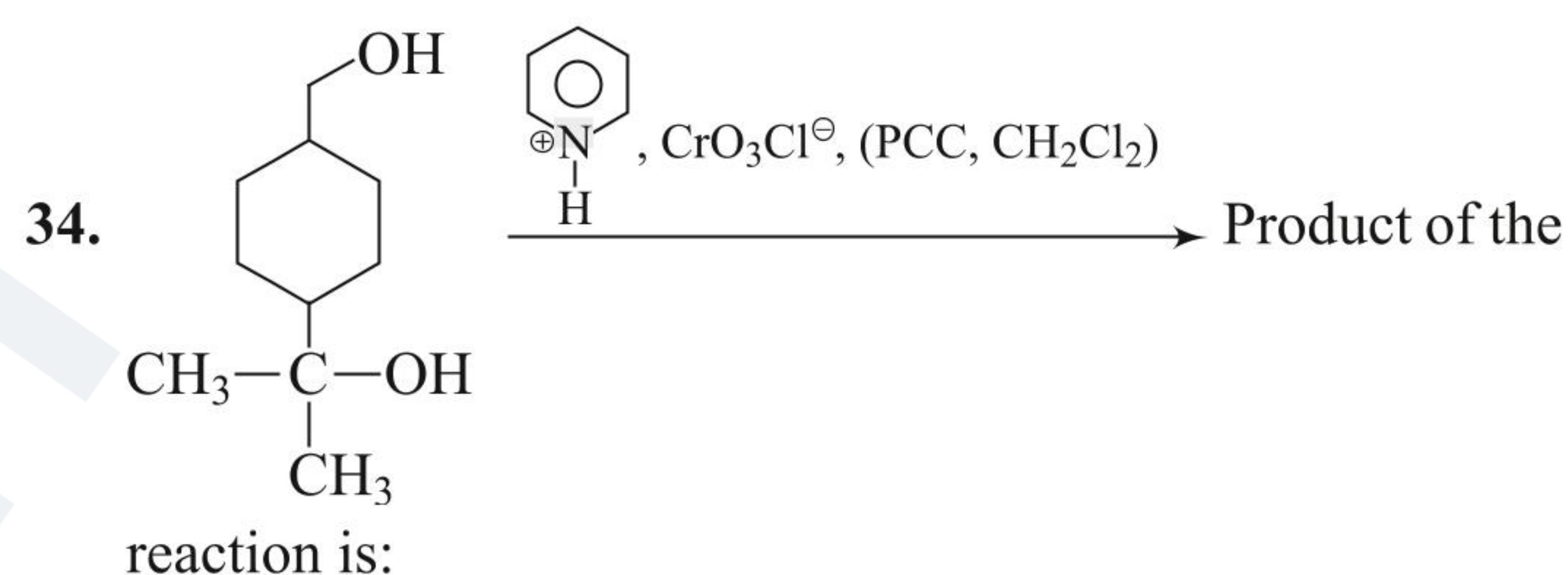
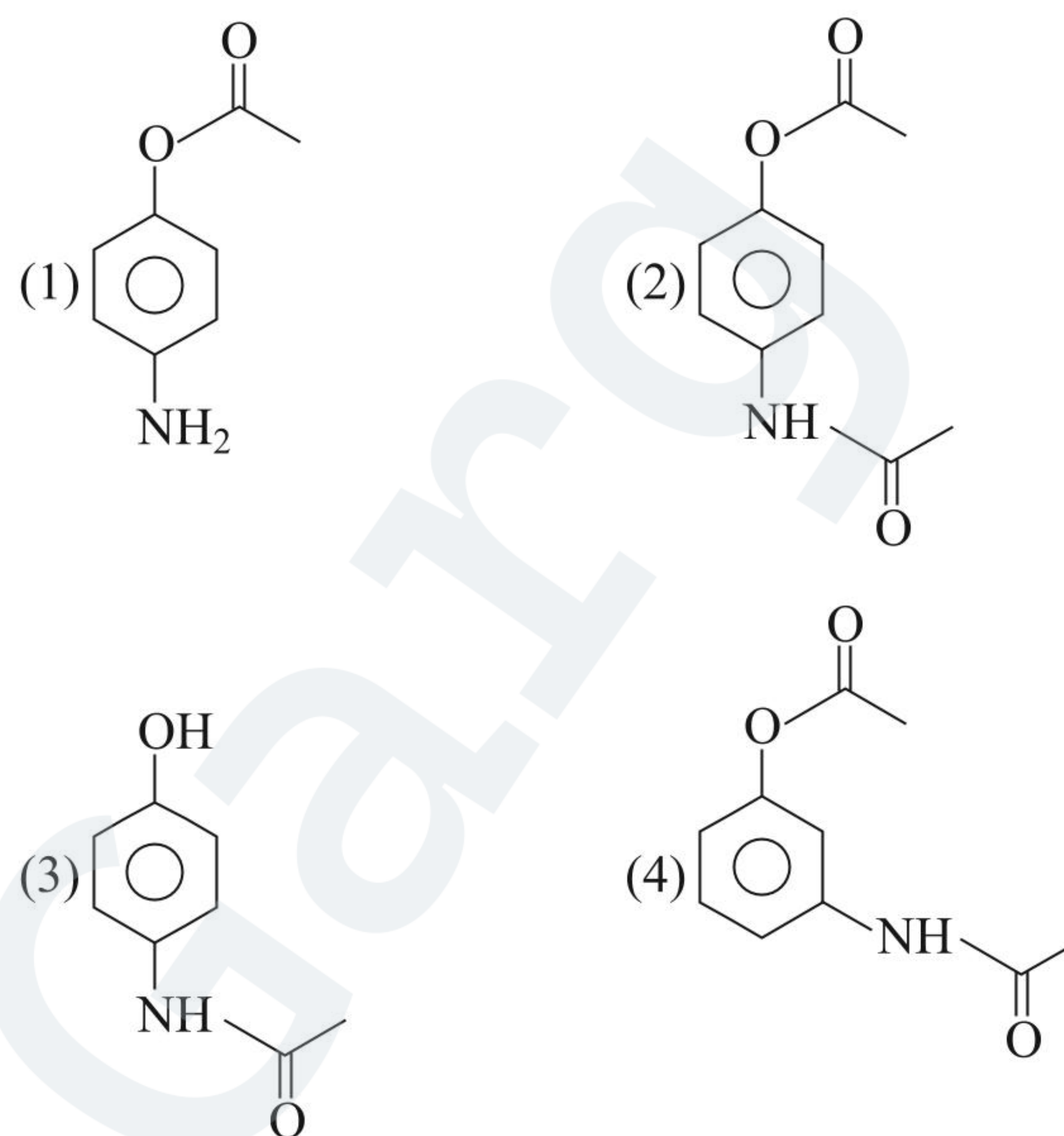
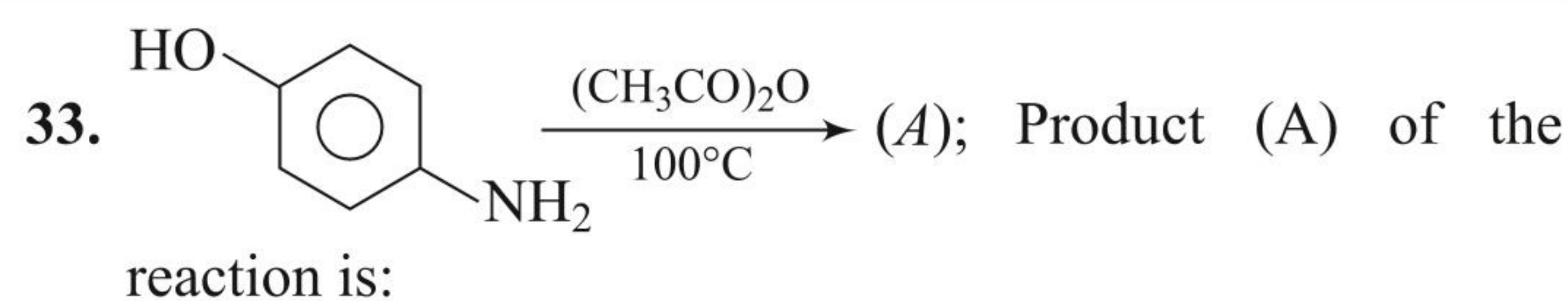
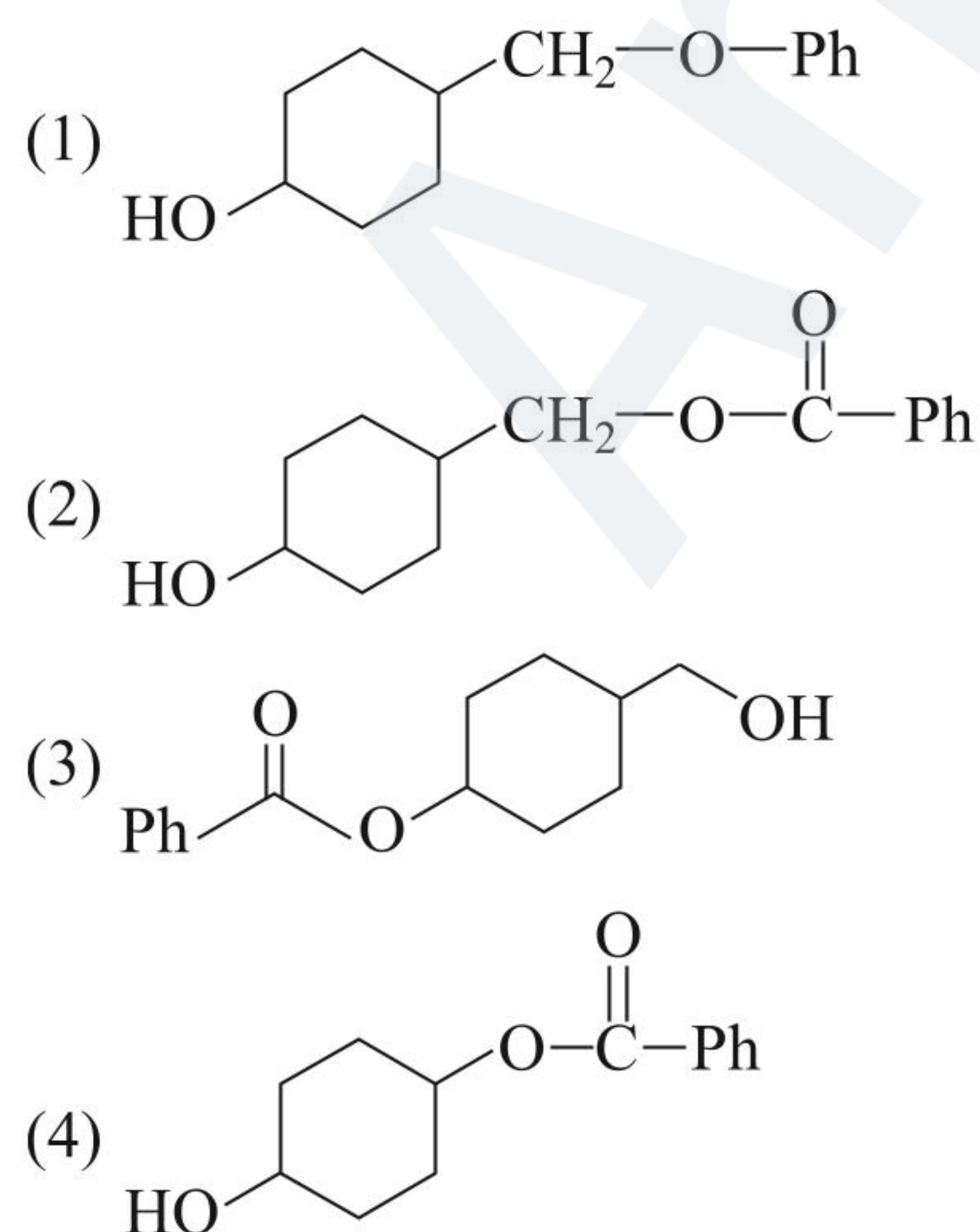


The order of decreasing reactivities of these alcohols towards nucleophilic substitution with HBr is:

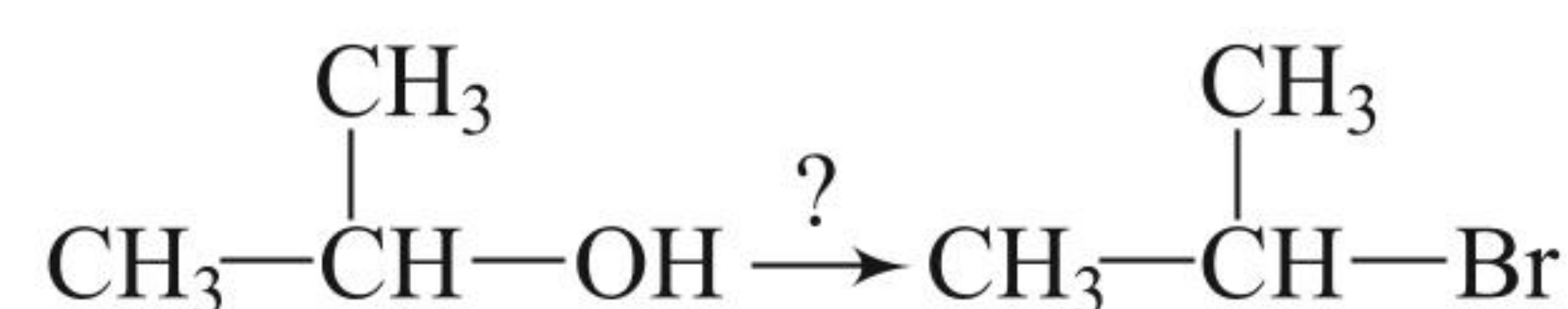
- (1) III > I > IV > II (2) III > I > II > IV
 (3) I > III > IV > II (4) I > III > II > IV



Major product of above esterification reaction is:

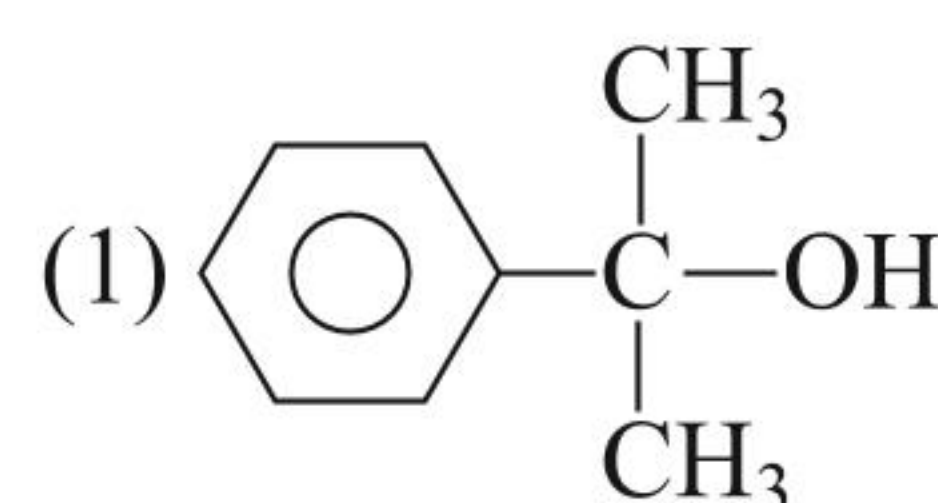


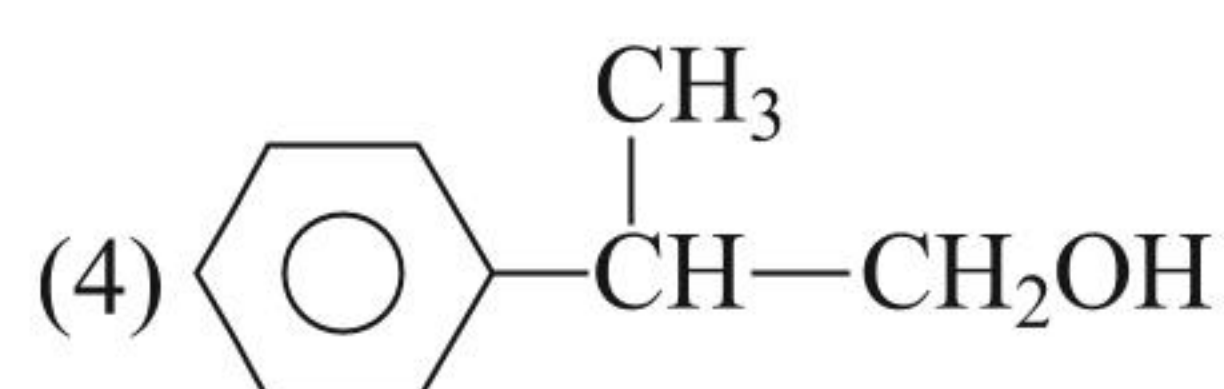
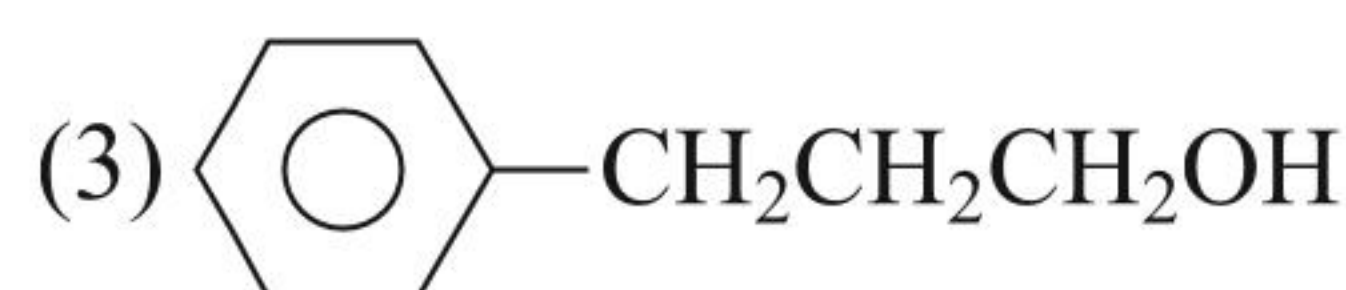
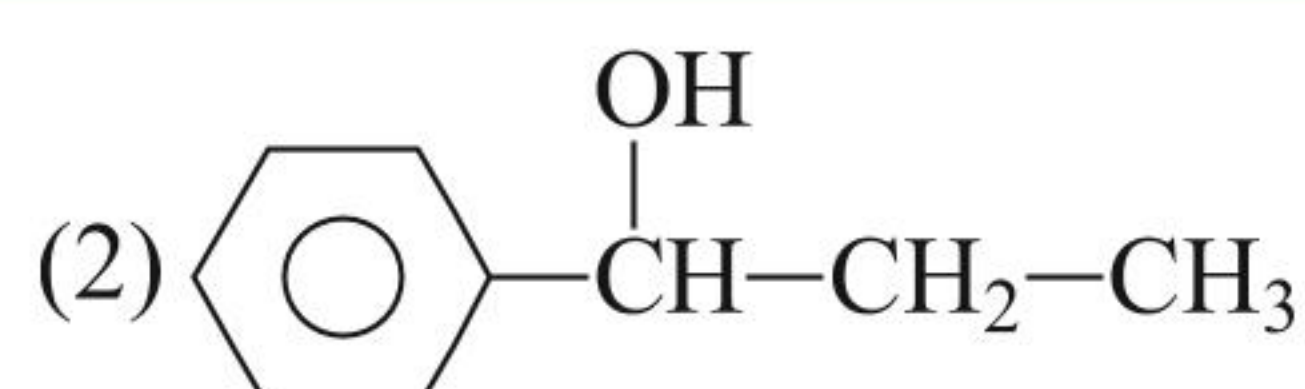
35. Which is the best reagent to convert isopropyl alcohol to isopropyl bromide?



- (1) Br₂ (2) SOBr₂
 (3) HBr (4) CH₃MgBr

36. An alcohol of formula C₉H₁₂O (A) reacts with Na₂Cr₂O₇ to form a compound having formula C₉H₁₀O. The original alcohol might be:

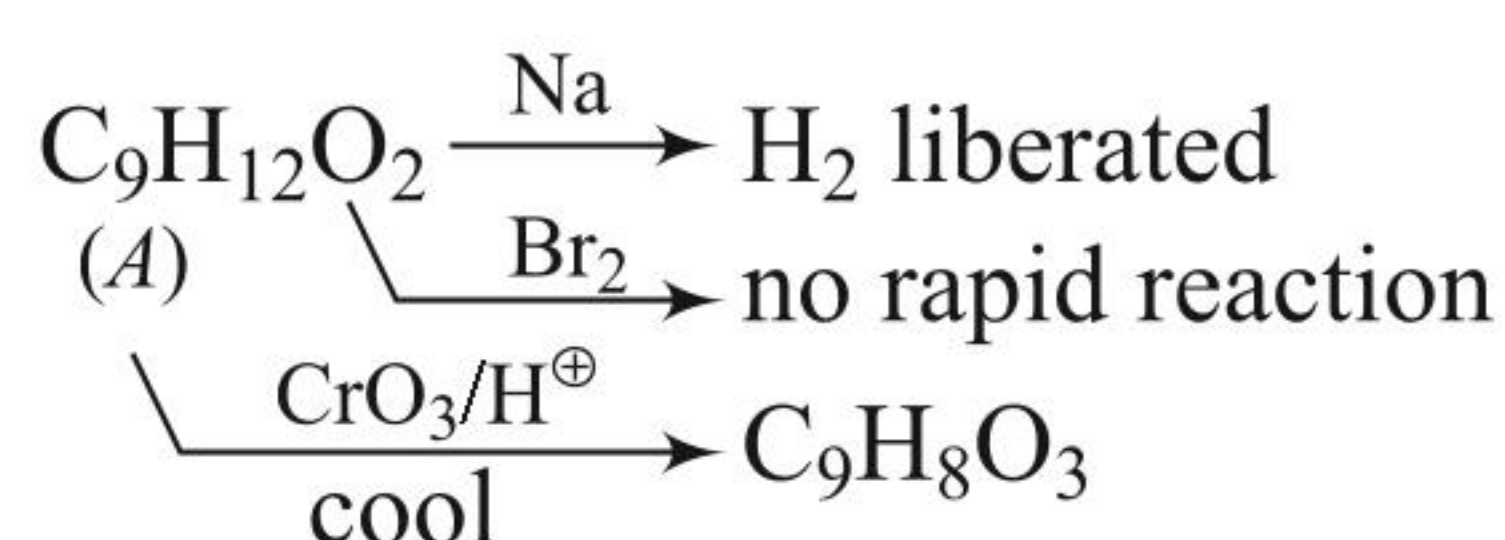




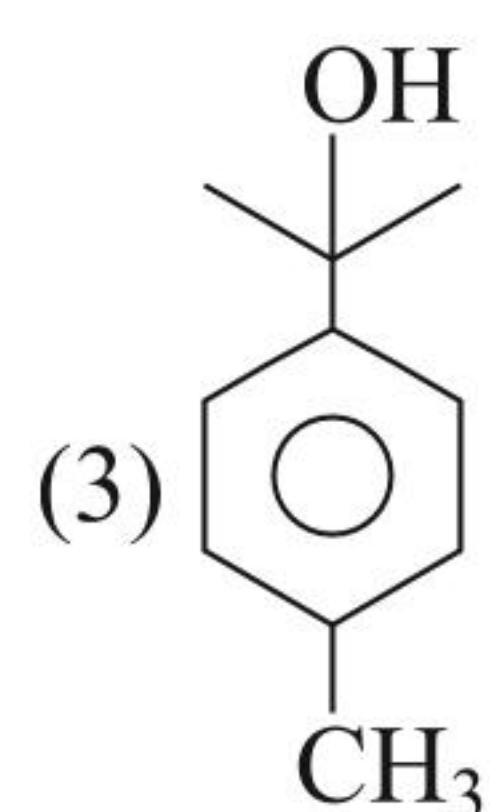
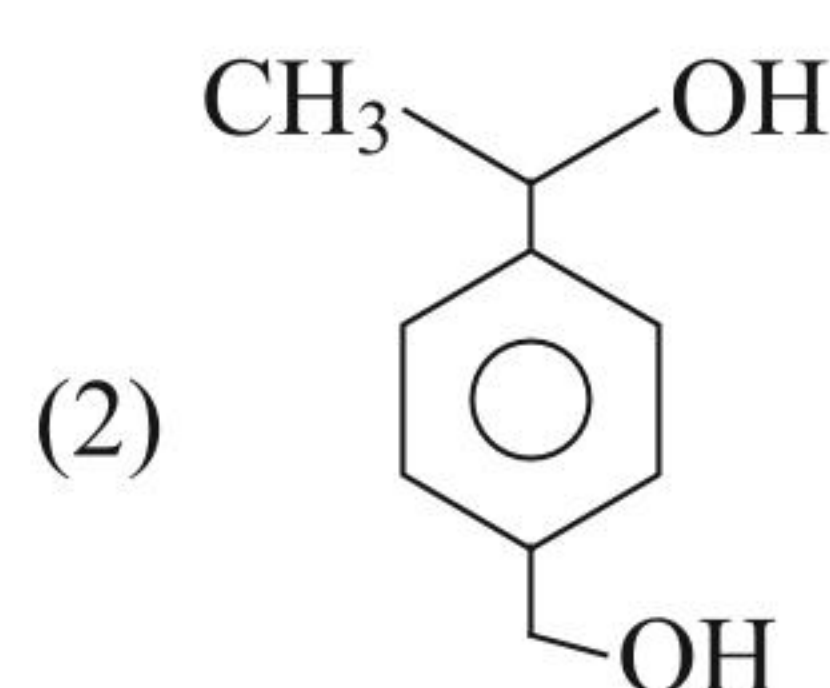
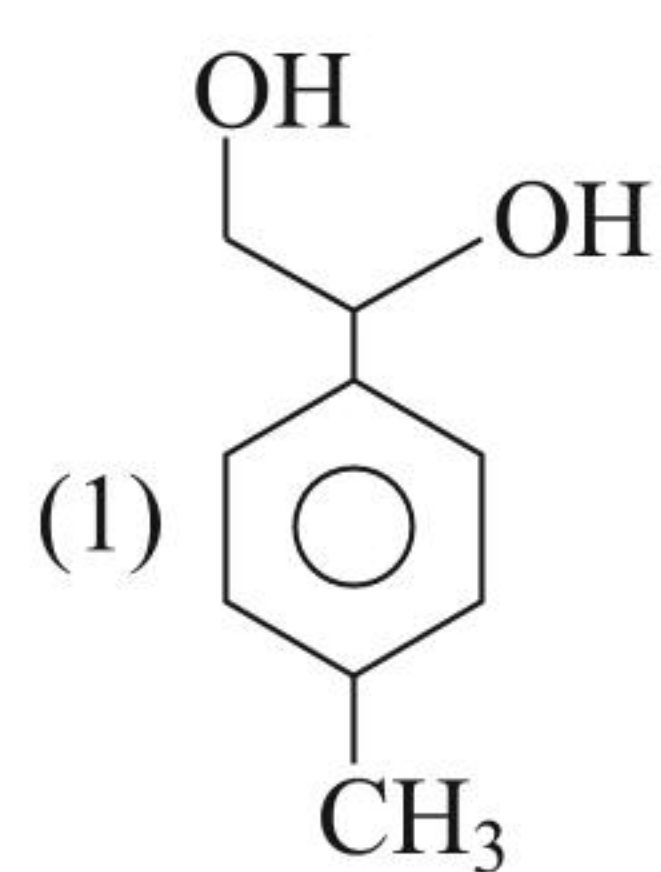
37. An optically active compound of formula $C_9H_{12}O_2$ produced the following compound when refluxed with $KMnO_4$.



The original compound showed these properties also:

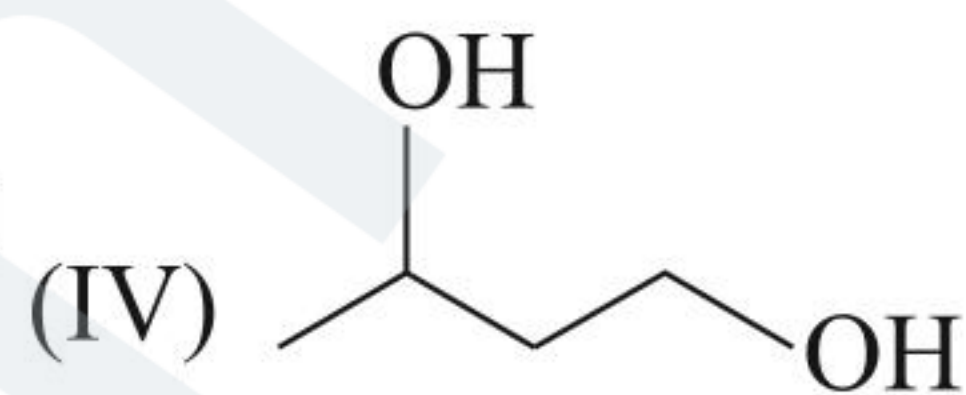
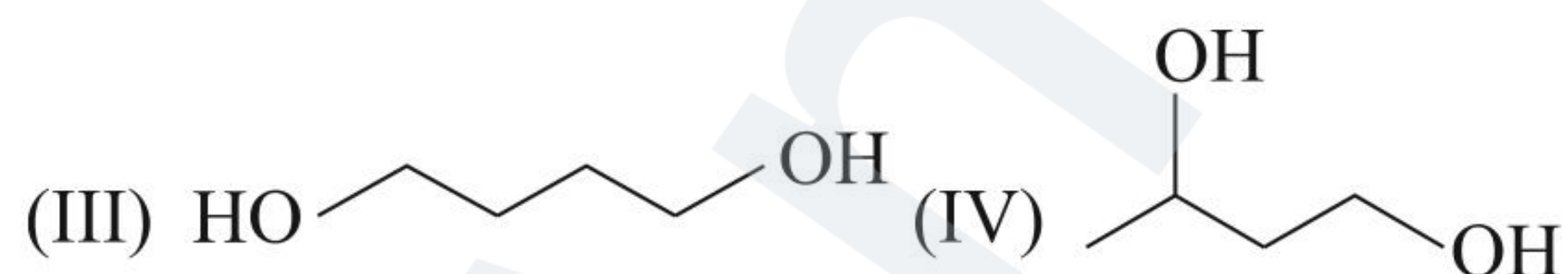
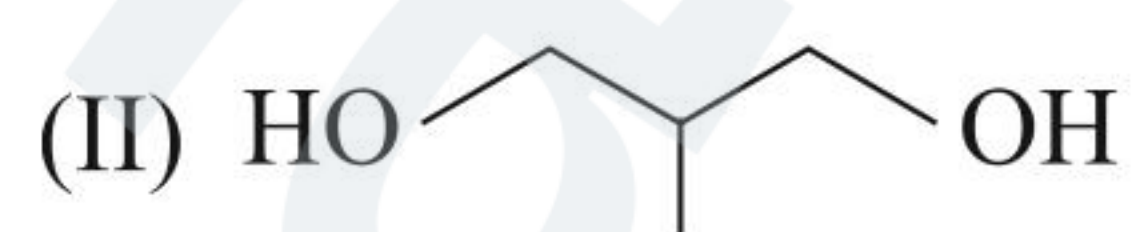
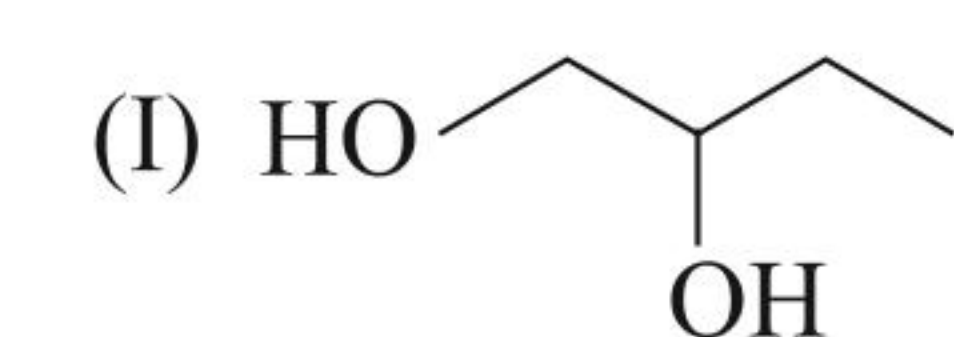


Which is structure of (A)?



(4) both (1) and (2)

38. Diols (I-IV) which react with CrO_3 in aqueous H_2SO_4 and yield products that readily undergo decarboxylation on heating are:



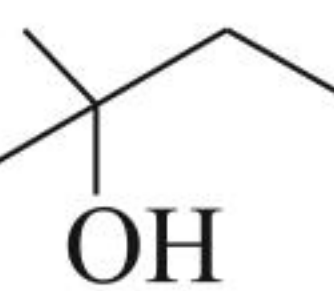
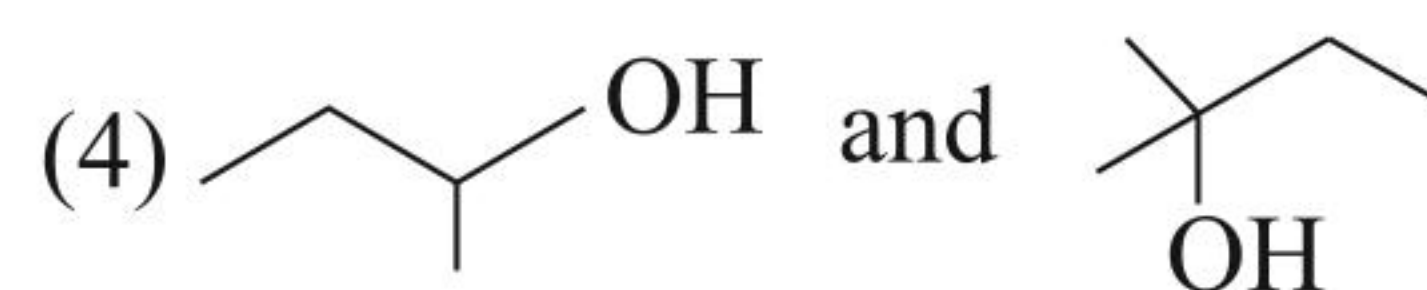
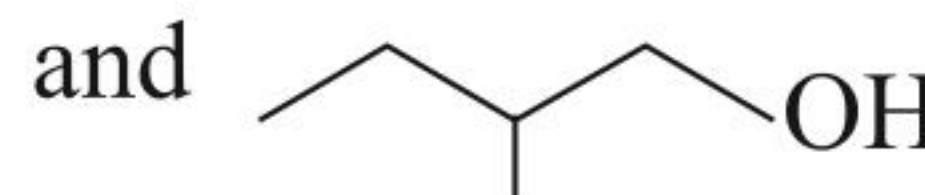
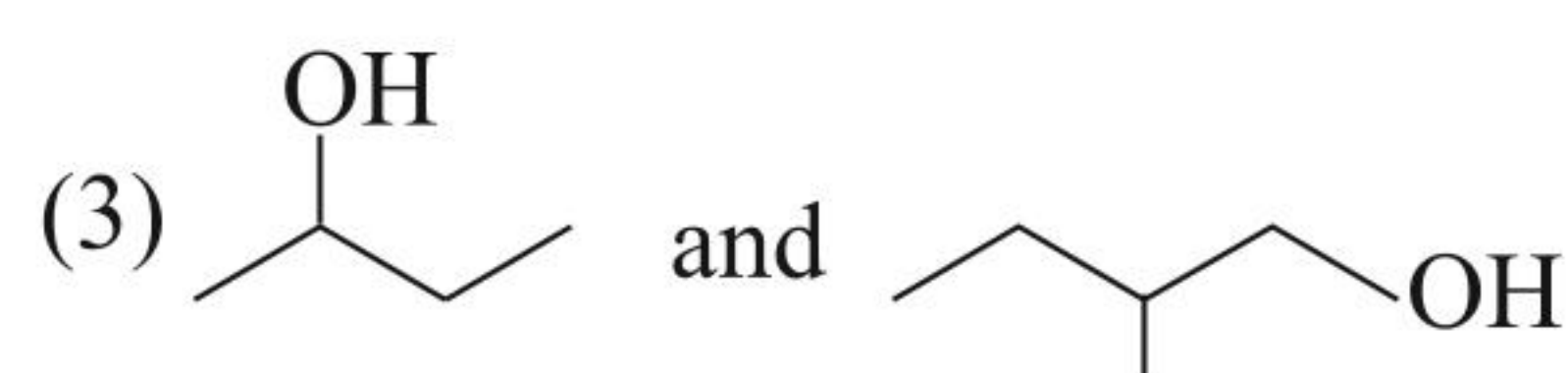
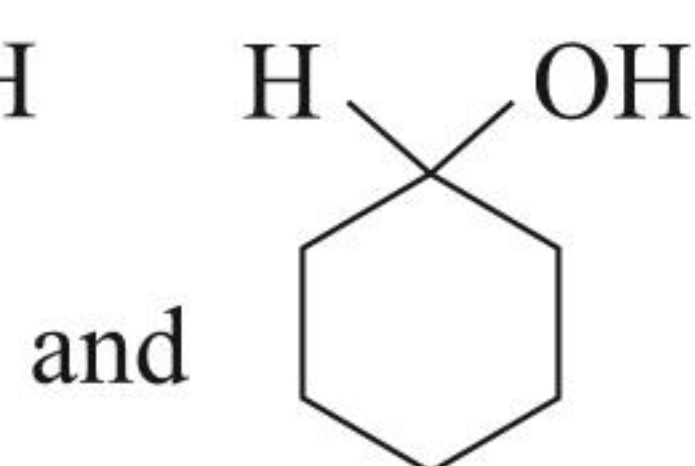
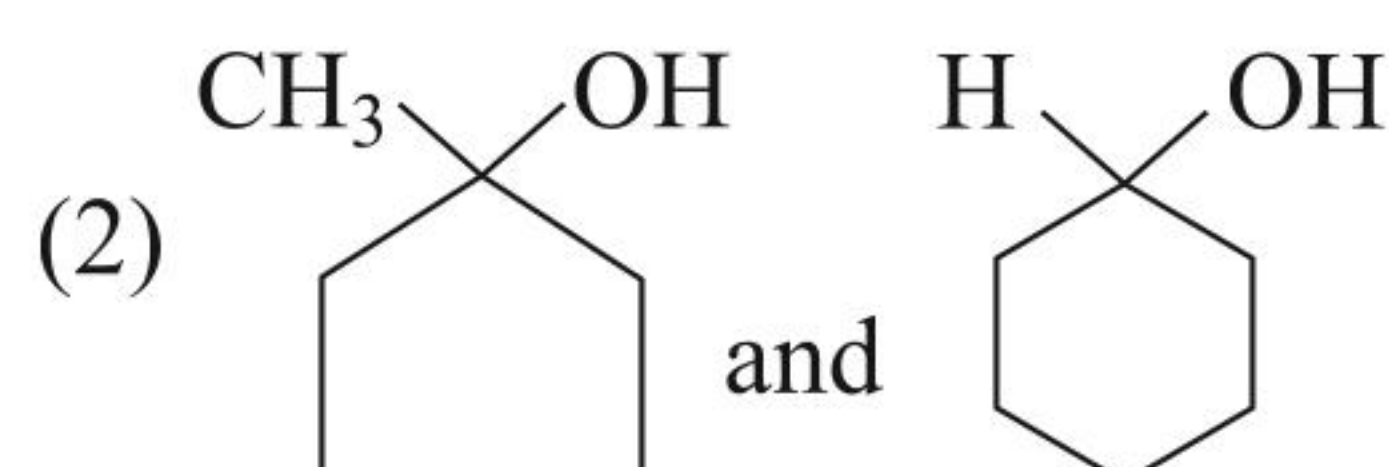
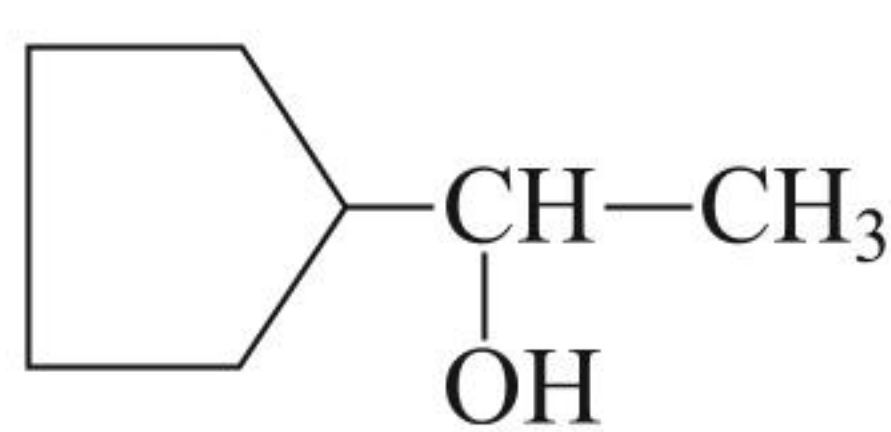
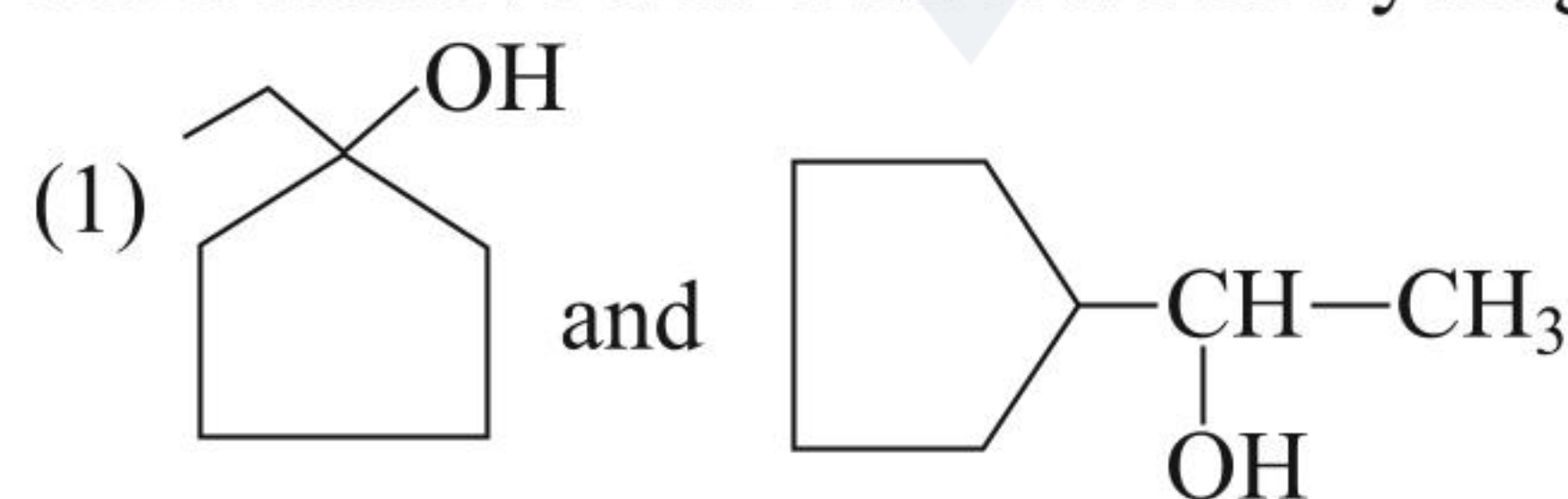
(1) I and II

(2) II and III

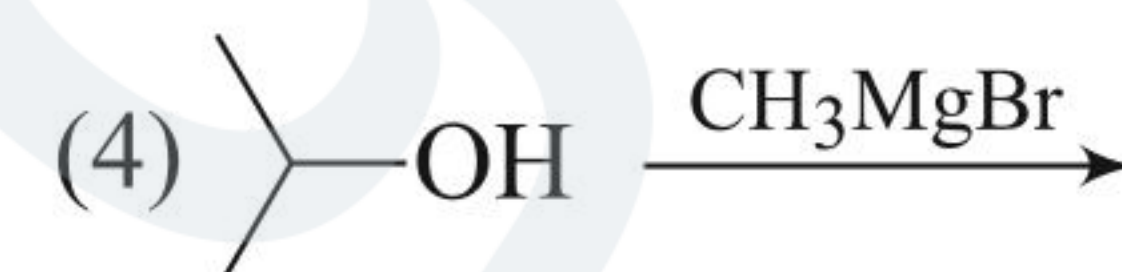
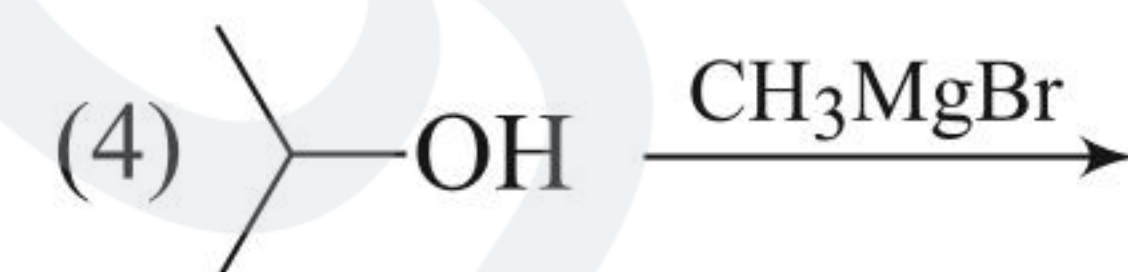
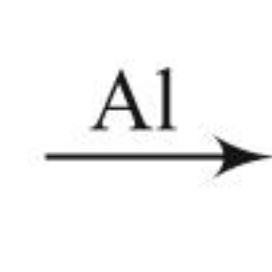
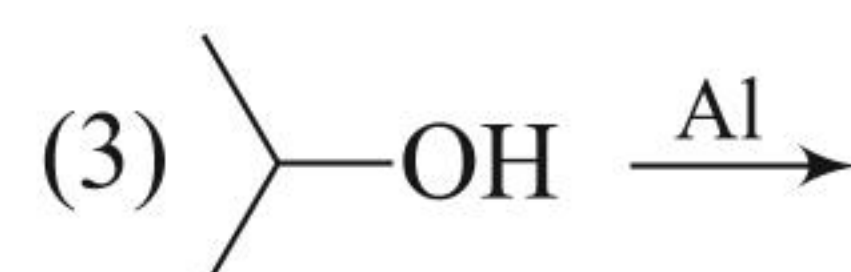
(3) II and IV

(4) I and IV

39. In the given pair of alcohol, in which pair second alcohol is more reactive than first towards hydrogen bromide?



40. In which of the following reactions hydrogen gas will not be evolved?



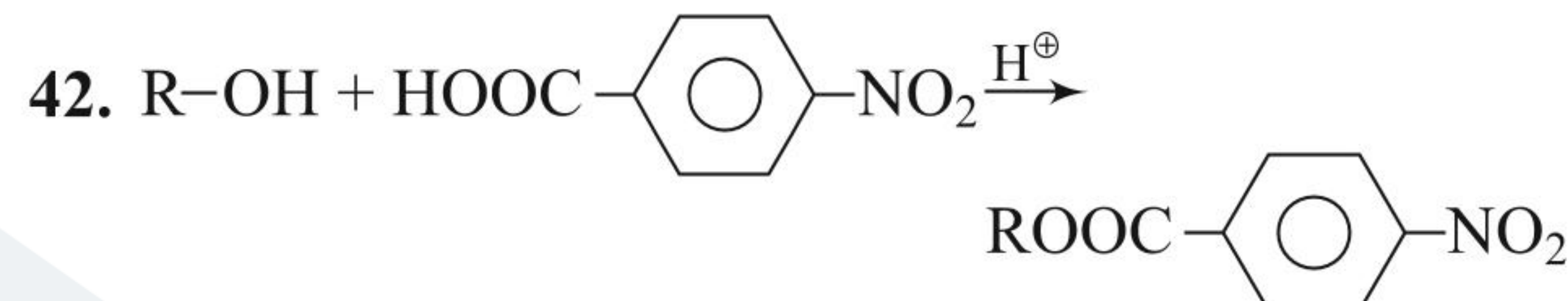
41. The major reason that phenol is a better Bronsted acid than cyclohexanol is that:

(1) the cyclohexyl group is an electron donating group by induction, which destabilizes the anion formed in the reaction by resonance.

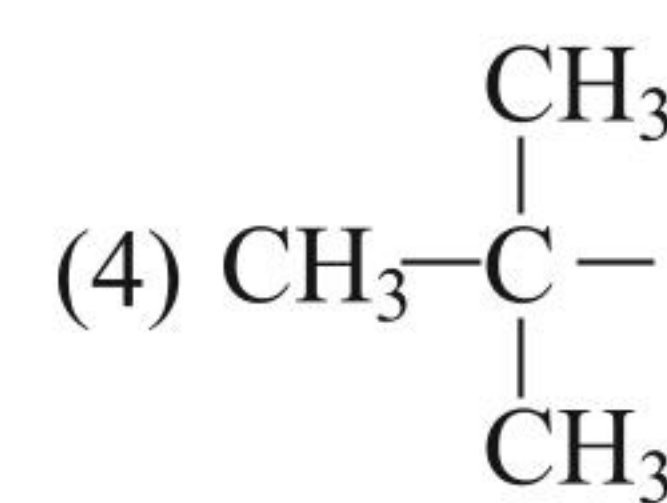
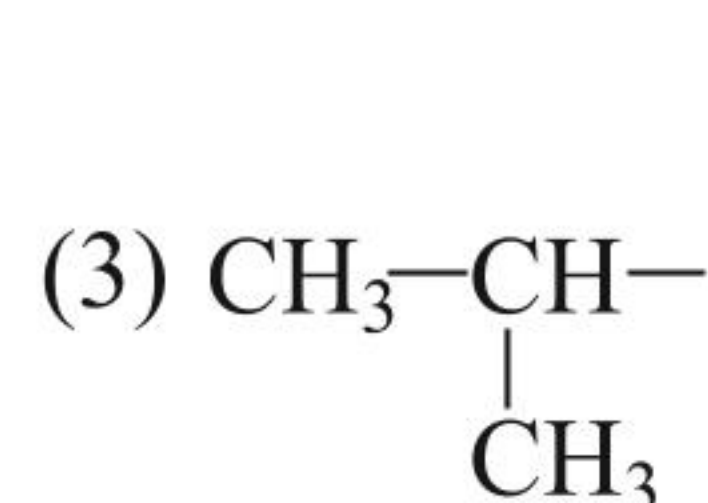
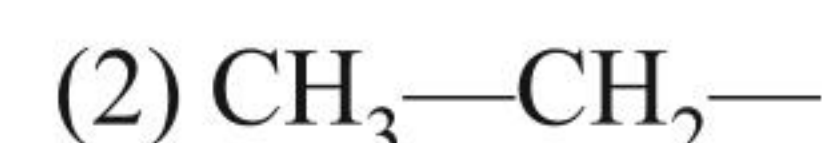
(2) phenol is able to stabilize the anion formed in the reaction.

(3) it is a better proton donor.

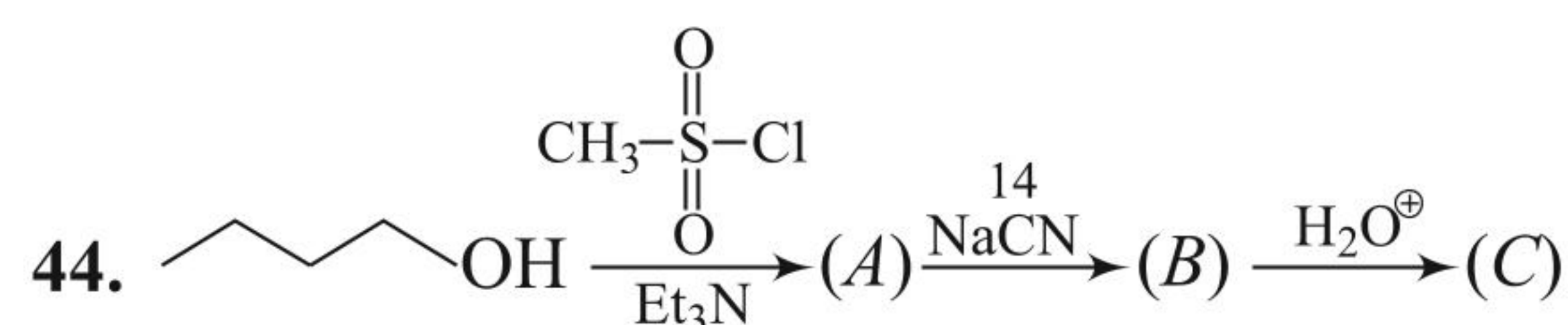
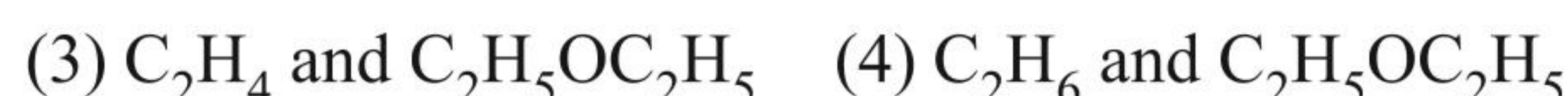
(4) the phenyl group is an electron withdrawing group by induction, which stabilizes the anion formed in the reaction.



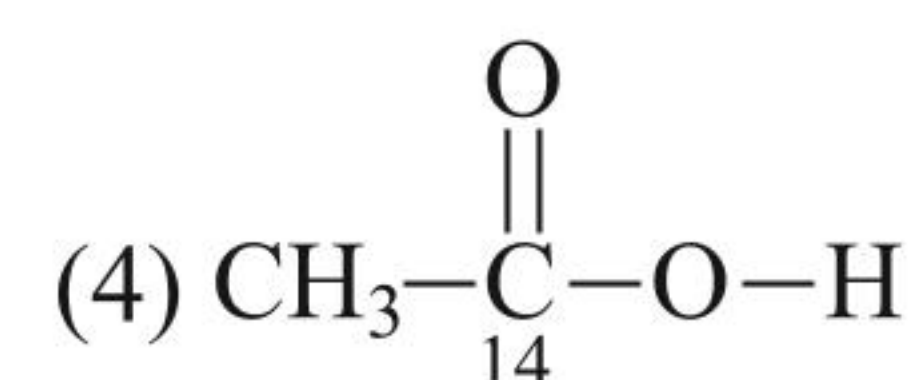
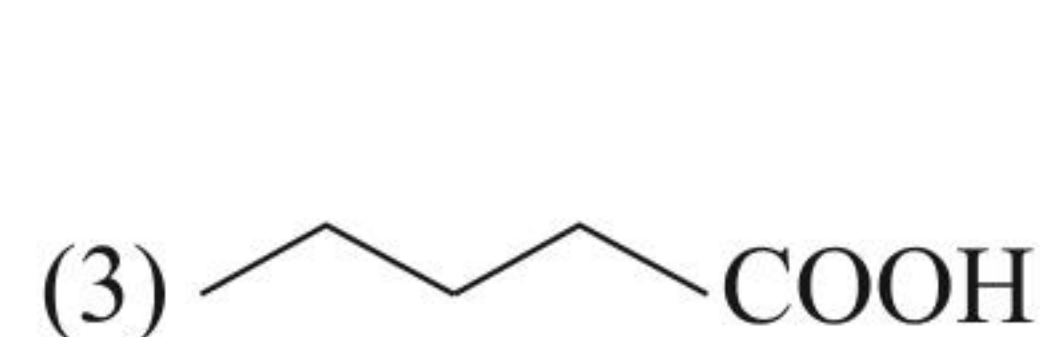
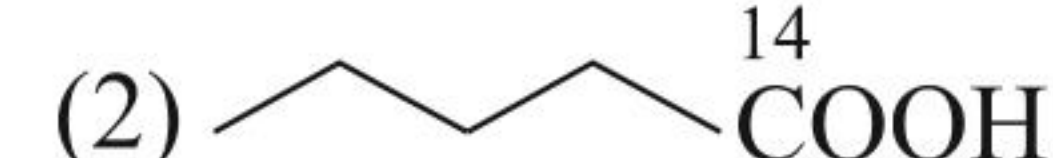
Fastest rate of reaction will be when R is:



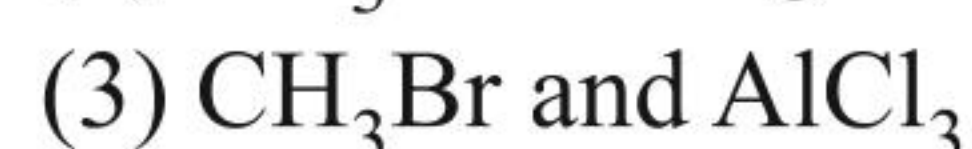
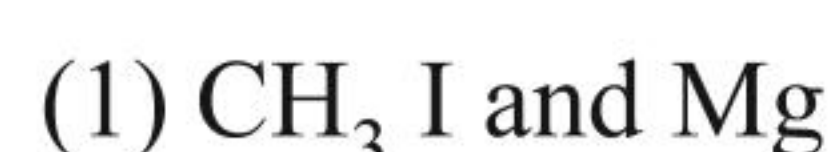
43. Ethanol when reacts with PCl_5 gives (A), $POCl_3$ and HCl (A) reacts with dry Ag_2O to form B (major product) and $AgCl$. A and B respectively are:



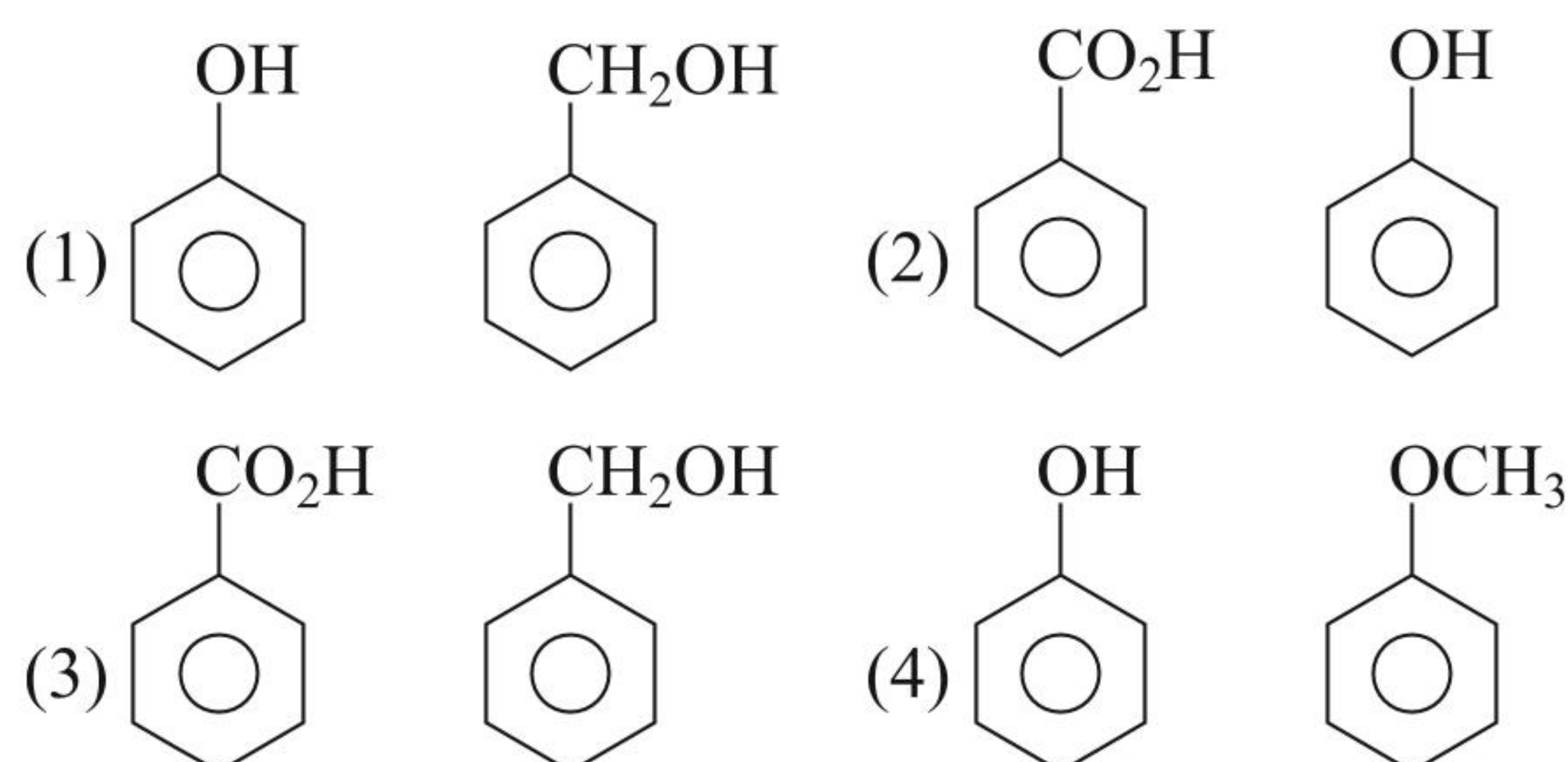
Product (C) is:



45. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with the product obtained in the reaction between:



46. Which of the following compounds is differentiated by NaHCO_3 as well as by NaOH ?

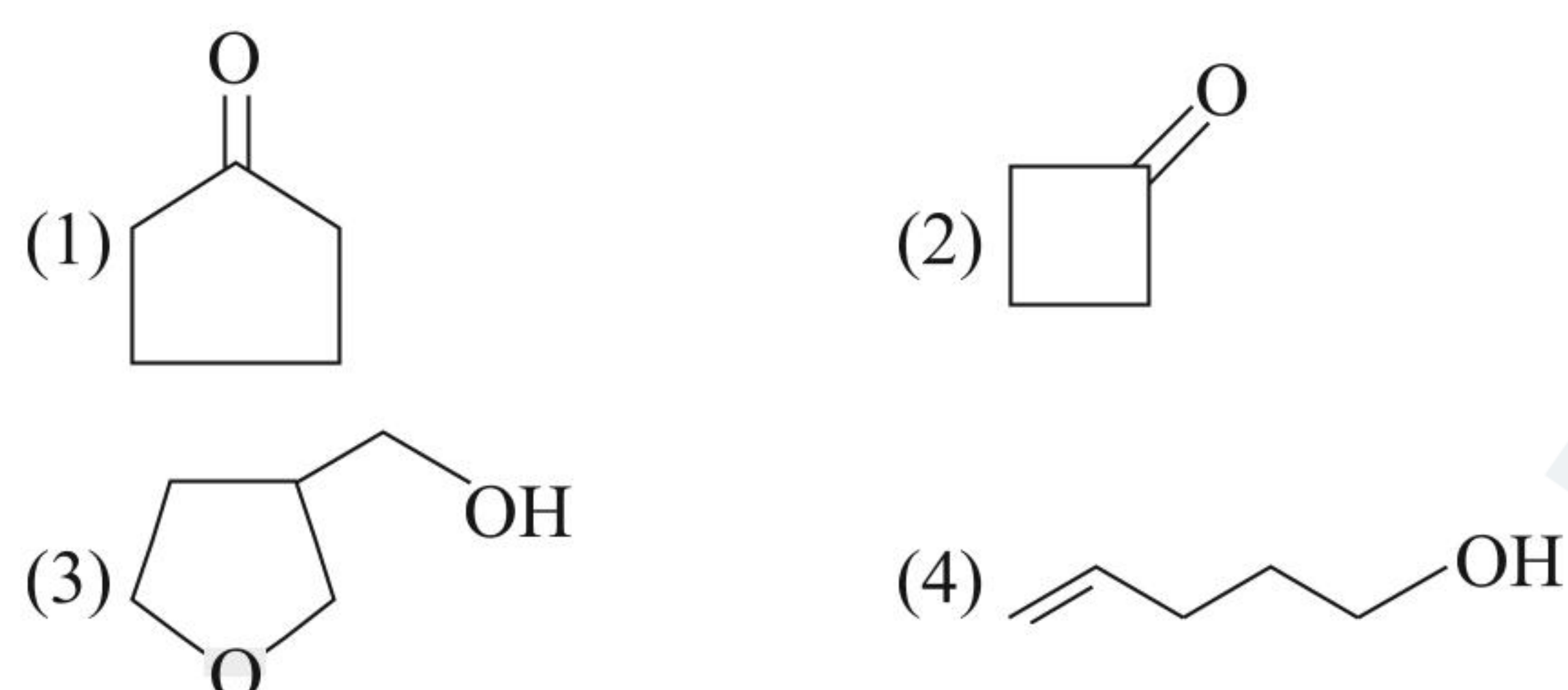


47. In the Libermann's nitroso reaction, sequential changes in the colour of phenol occurs as:

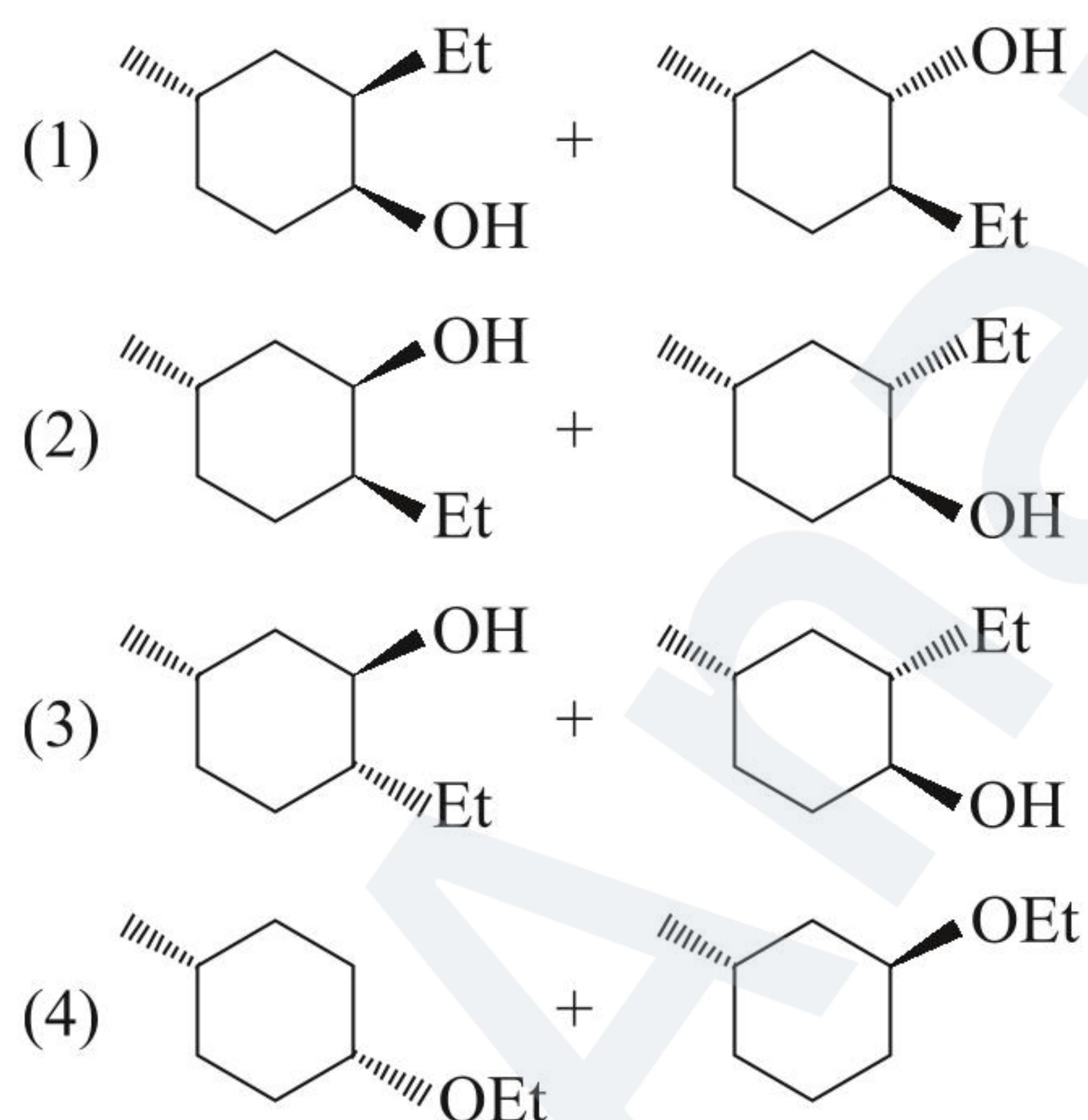
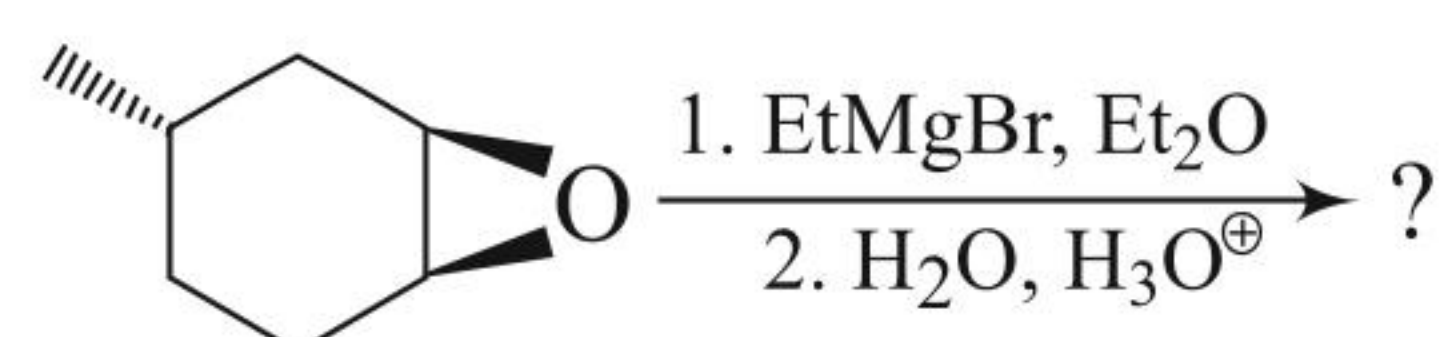
- (1) Brown or red \rightarrow green \rightarrow deep blue
- (2) Red \rightarrow deep blue \rightarrow green
- (3) Red \rightarrow green \rightarrow Colourless
- (4) White \rightarrow red \rightarrow green

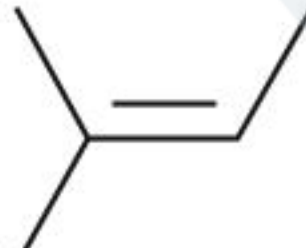
48. (A) $(\text{C}_4\text{H}_8\text{O}) \xrightarrow{\text{H}_3\text{O}^+} \text{(B)} \xrightarrow[\text{acetic acid}]{\text{CrO}_3} \text{(C)} \xrightarrow[\Delta]{\text{CH}_2\text{N}_2} \text{(D)}$

The compound (D) is

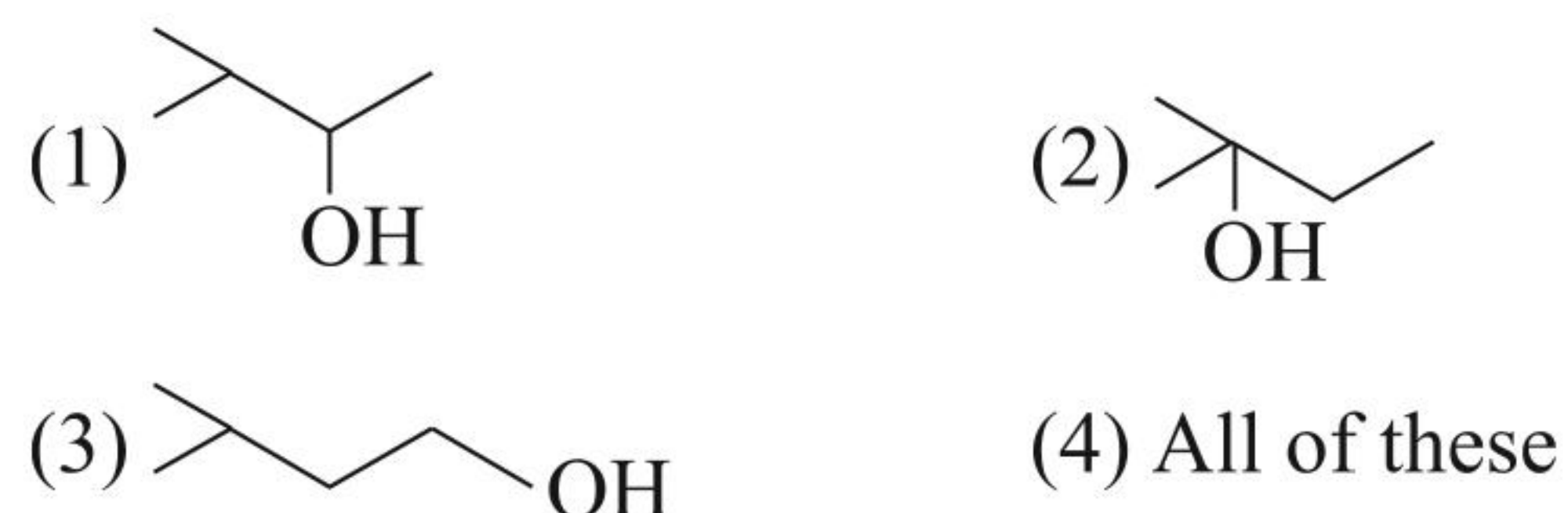



49. What are the major products of the following reaction?

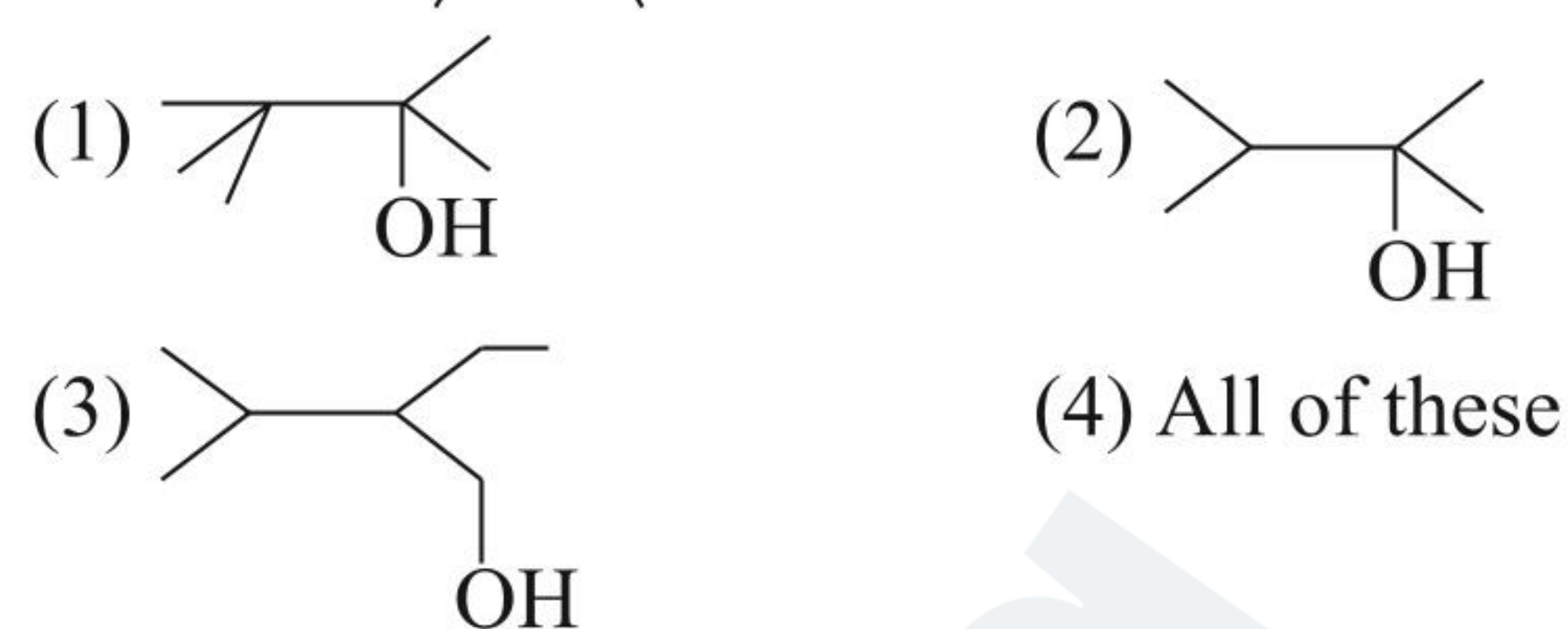


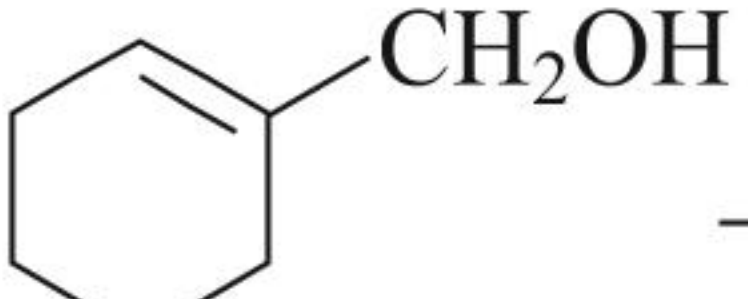
50. (A) $\xrightarrow[\Delta]{\text{H}^+}$ 

Structure of (A) is:



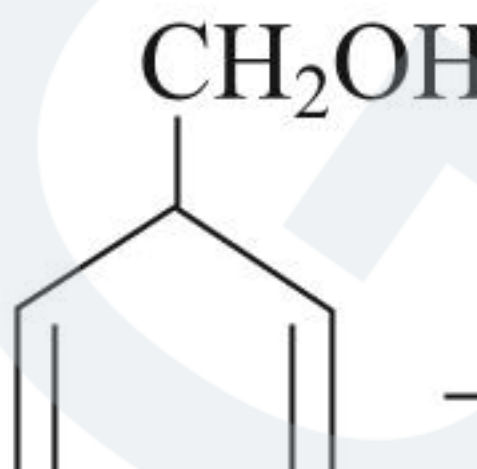
51. (A) $\xrightarrow[\Delta]{\text{H}^+}$ 



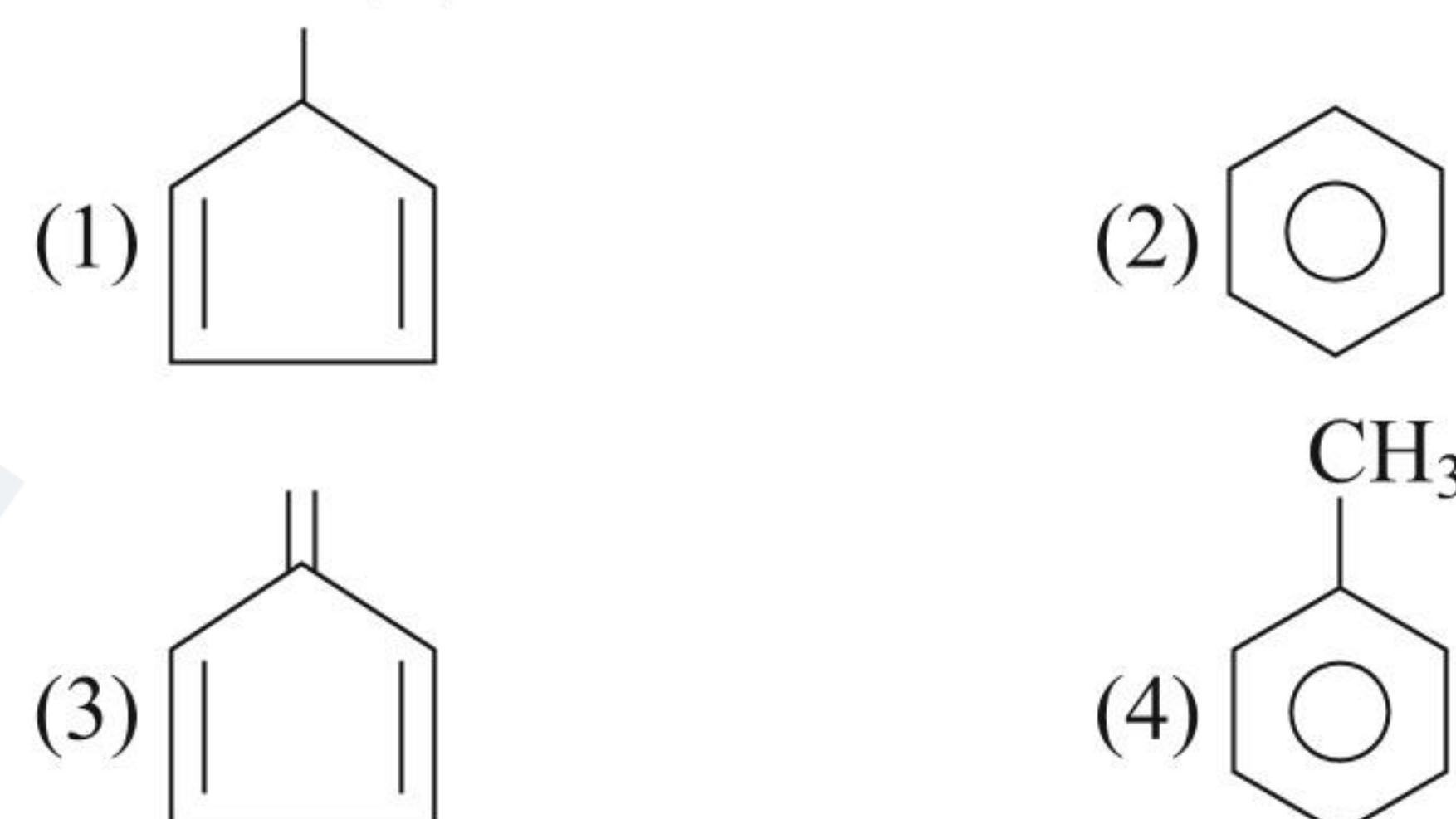
52.  $\xrightarrow[\Delta]{\text{H}^+}$ (A)

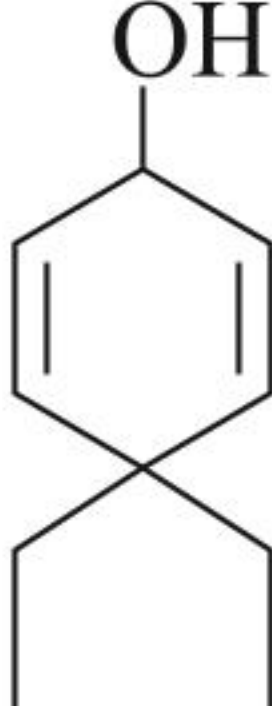
Product (A) is:

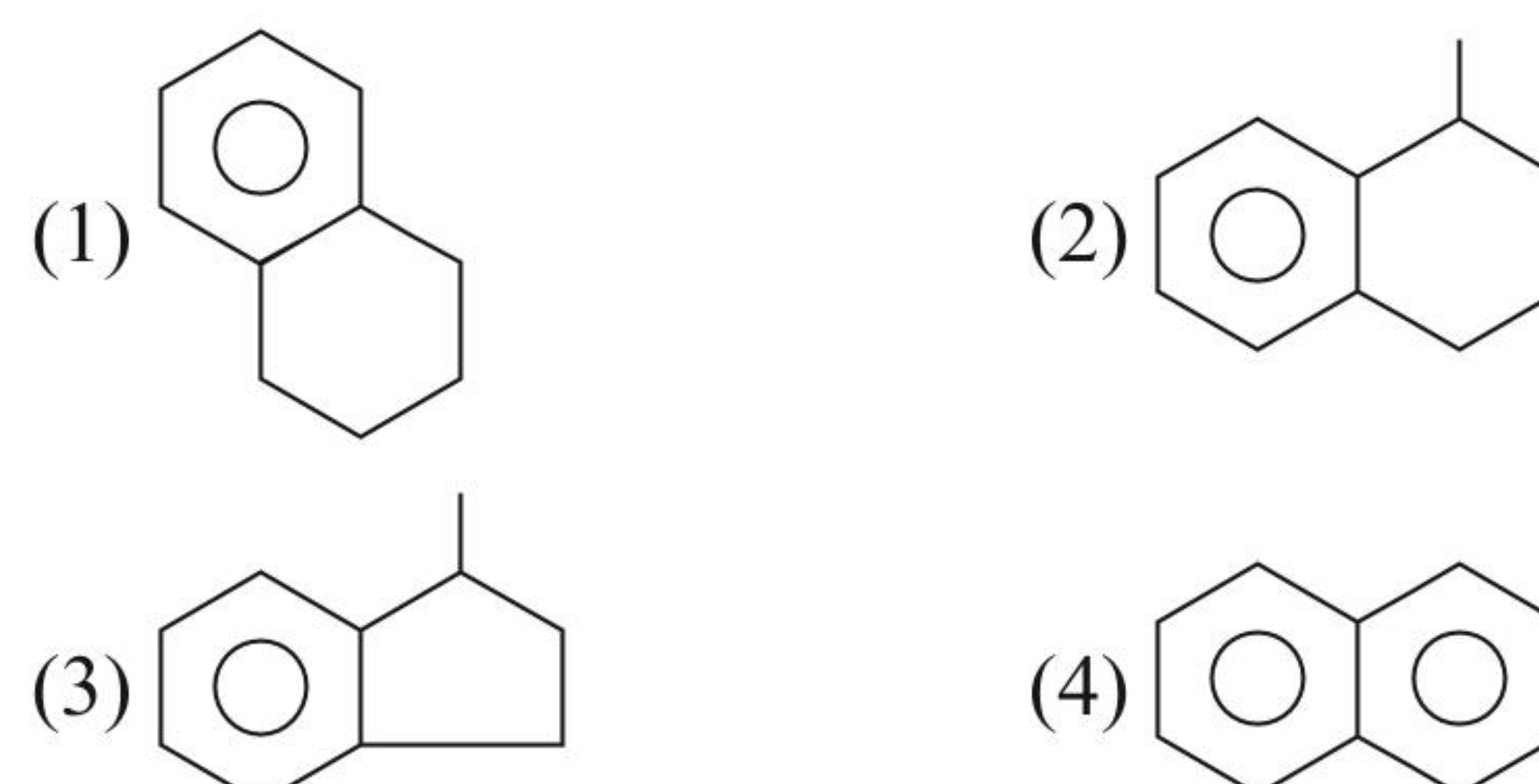


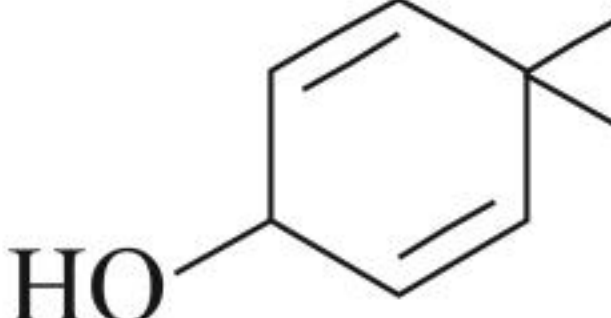
53.  $\xrightarrow[\Delta]{\text{H}^+}$ (A)

Product (A) is:



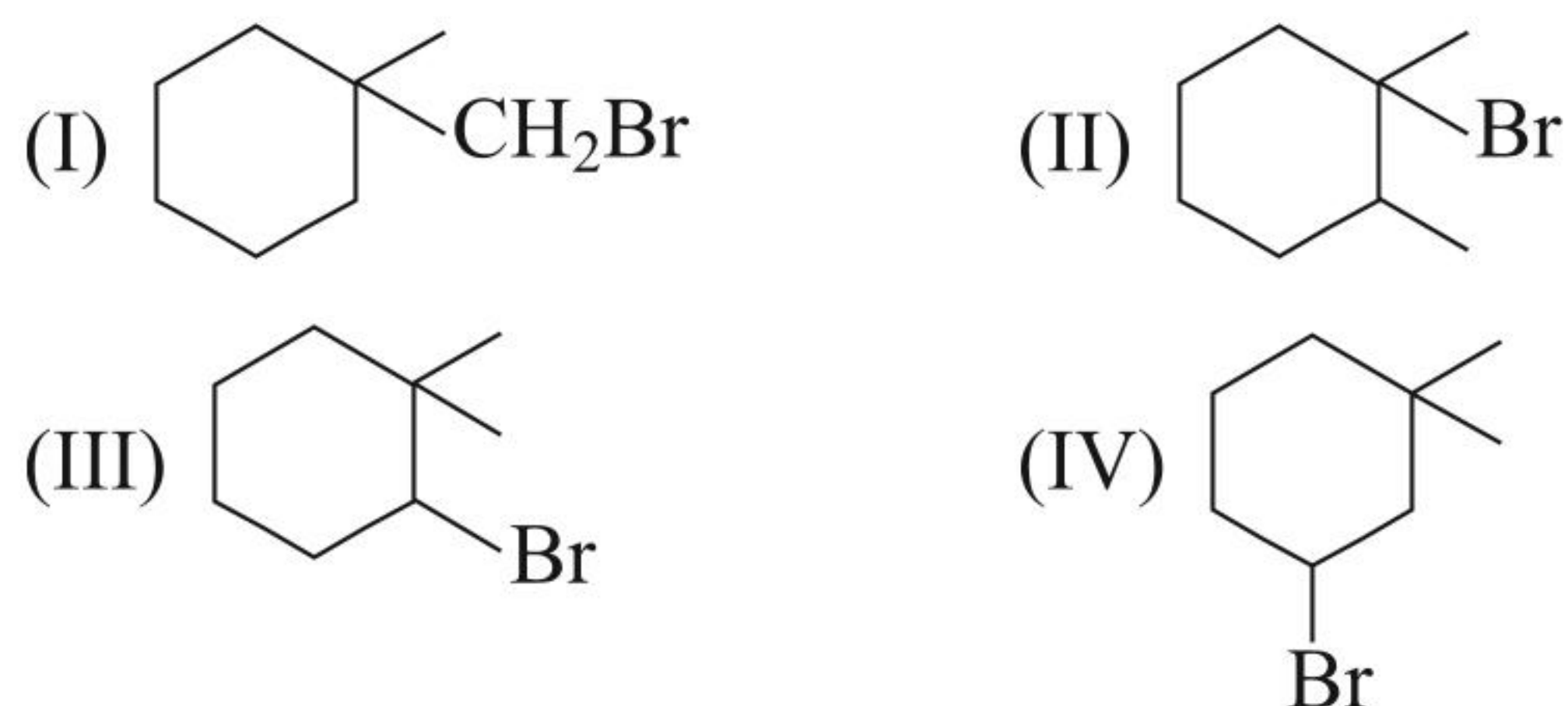
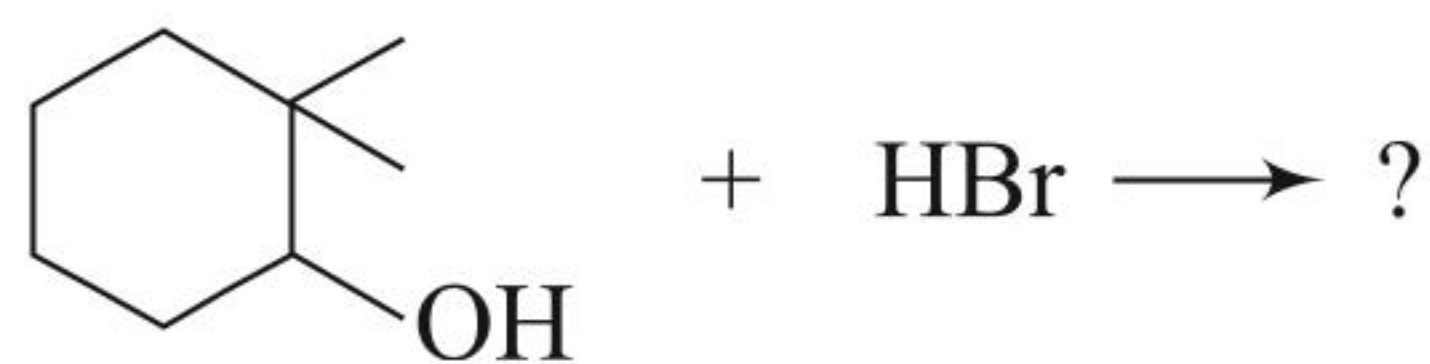
54.  $\xrightarrow[\Delta]{\text{H}^+}$ (A); Product (A) is:



55.  $\xrightarrow[\Delta]{\text{H}^+}$ (A); Product (A) is:



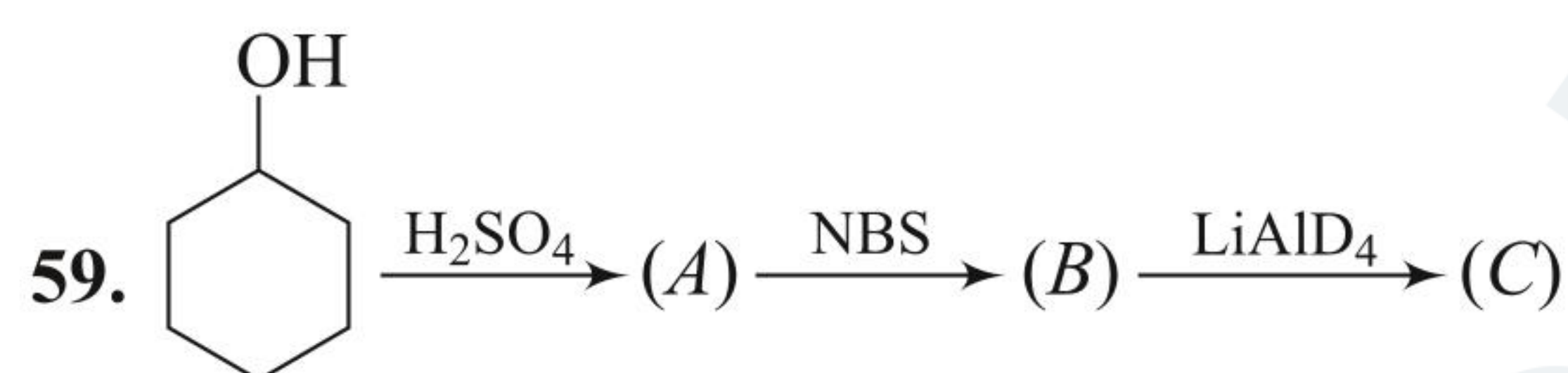
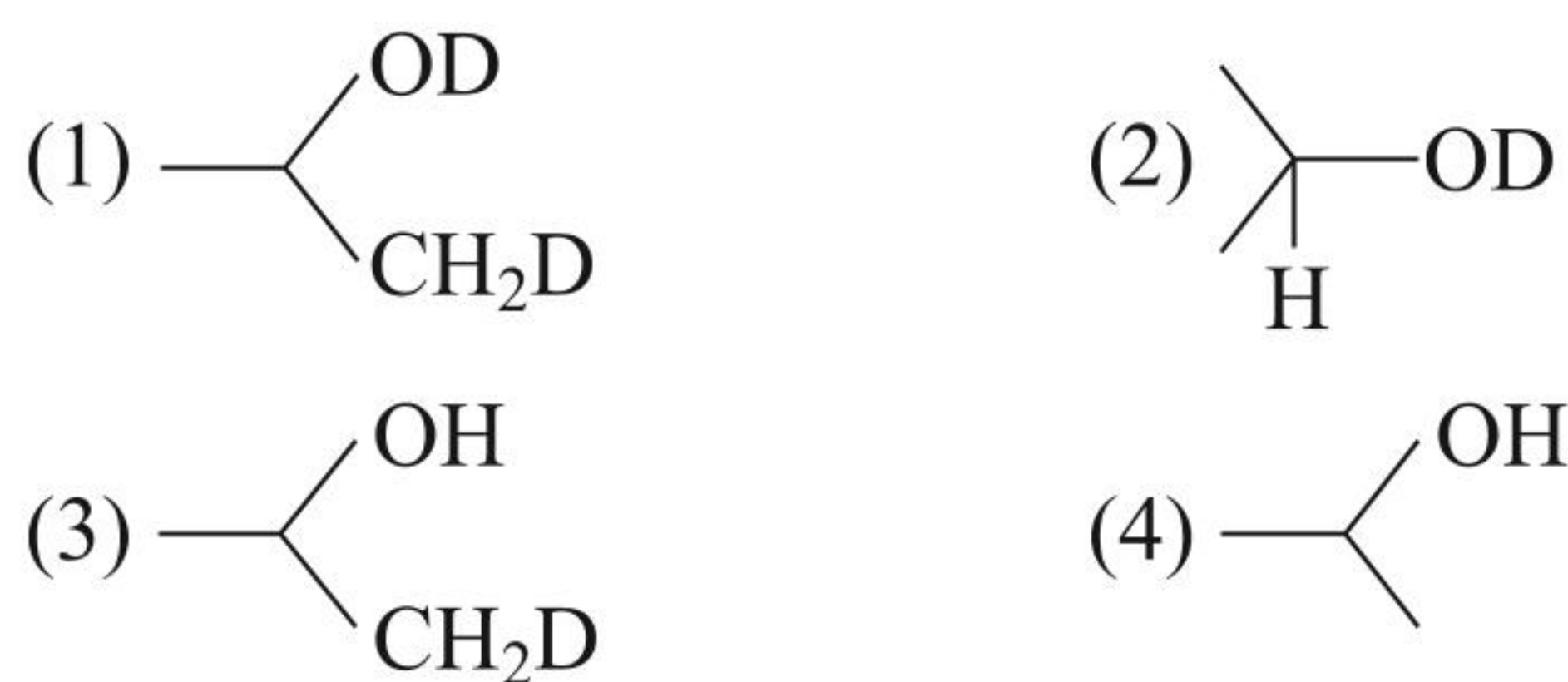
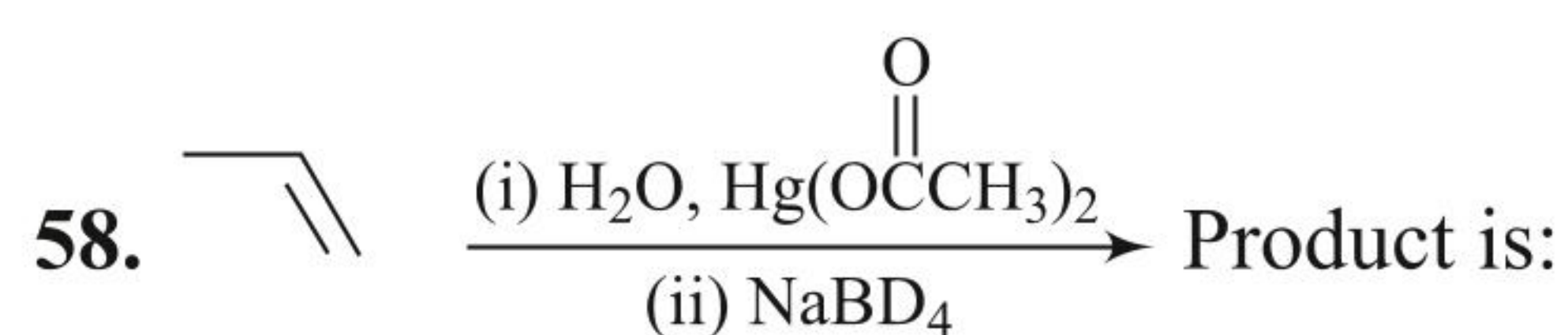
56. What is the major product of the following reaction?



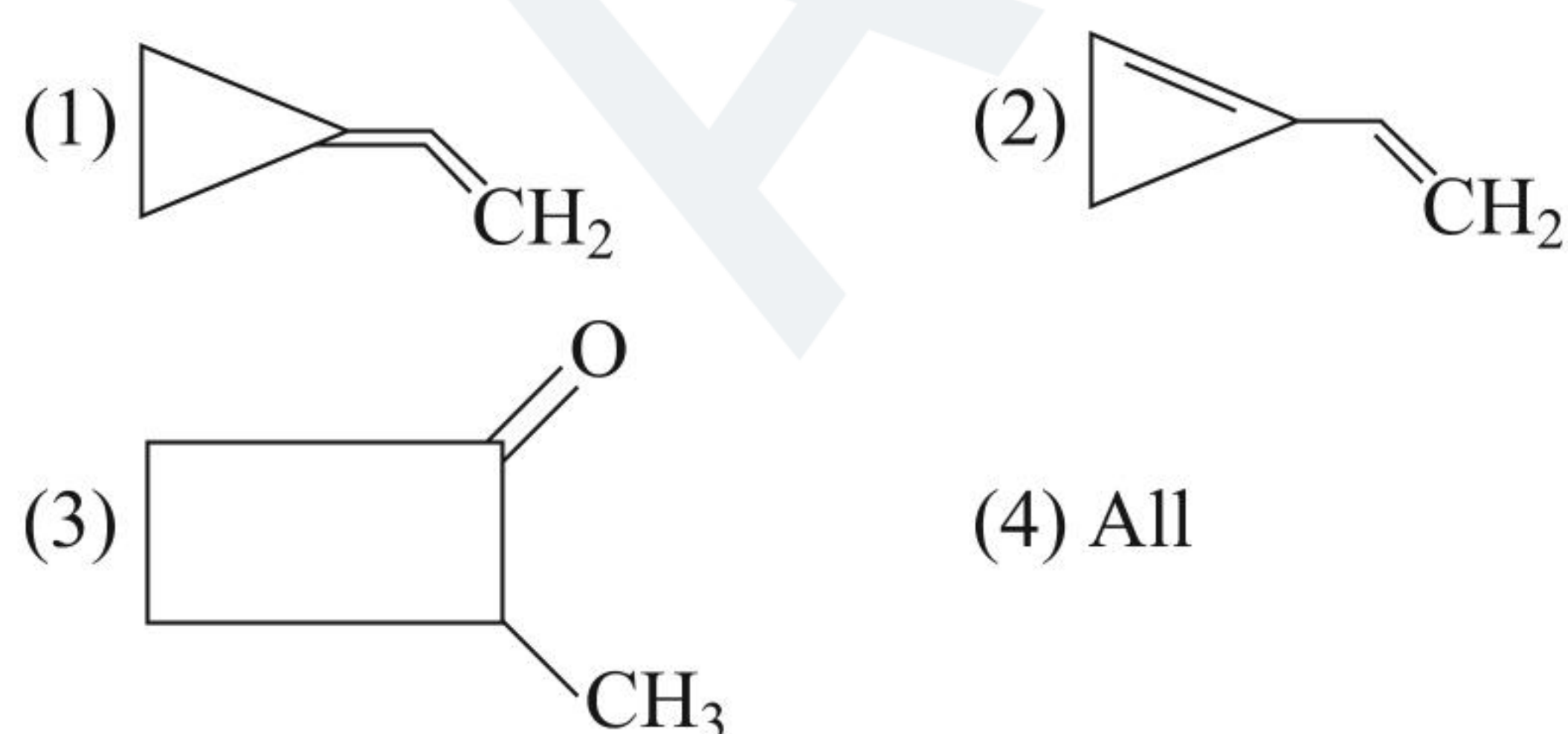
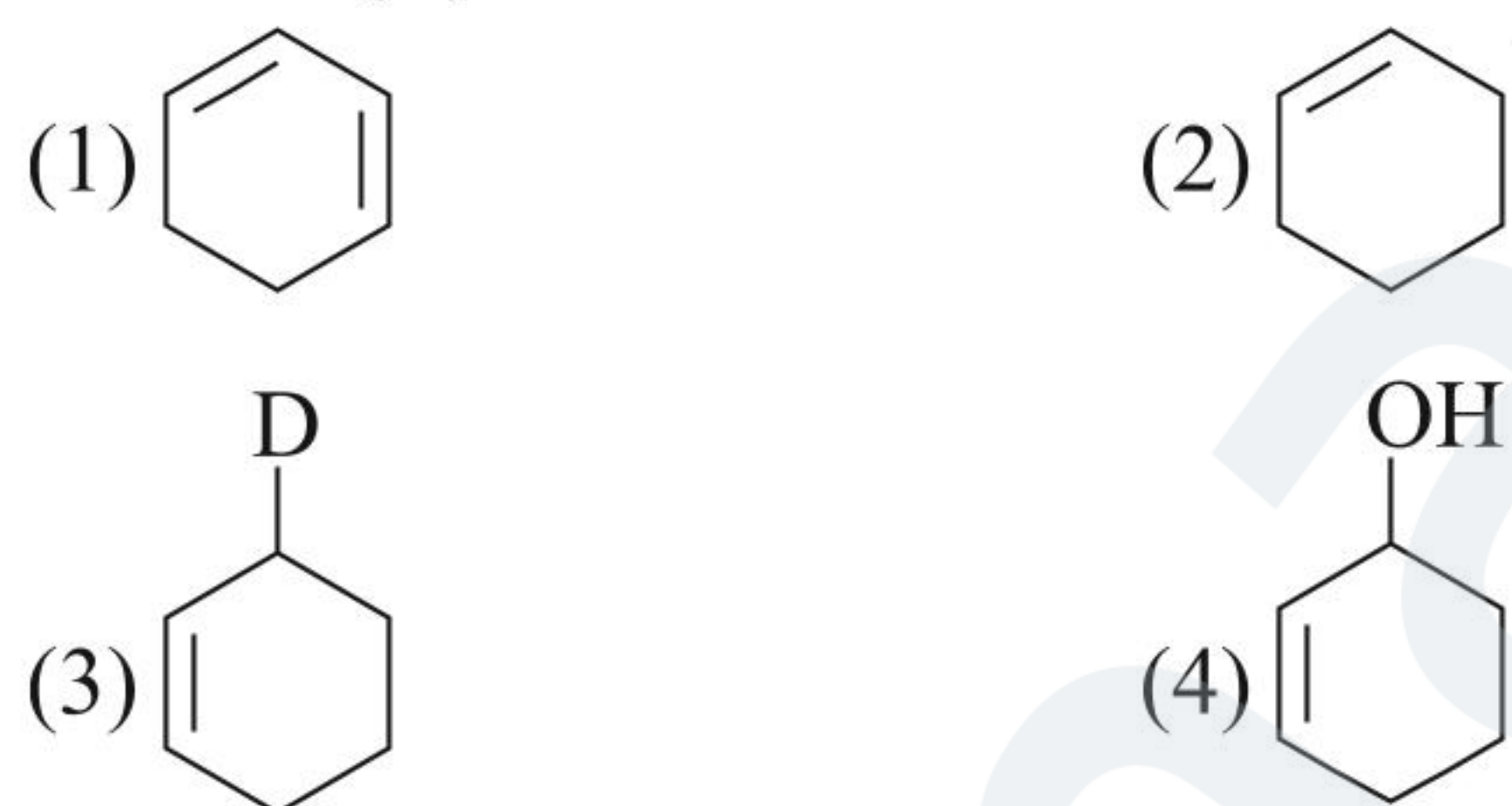
- (1) I (2) II
(3) III (4) IV

57. In the chromic acid oxidation of alcohols, the chromium is:

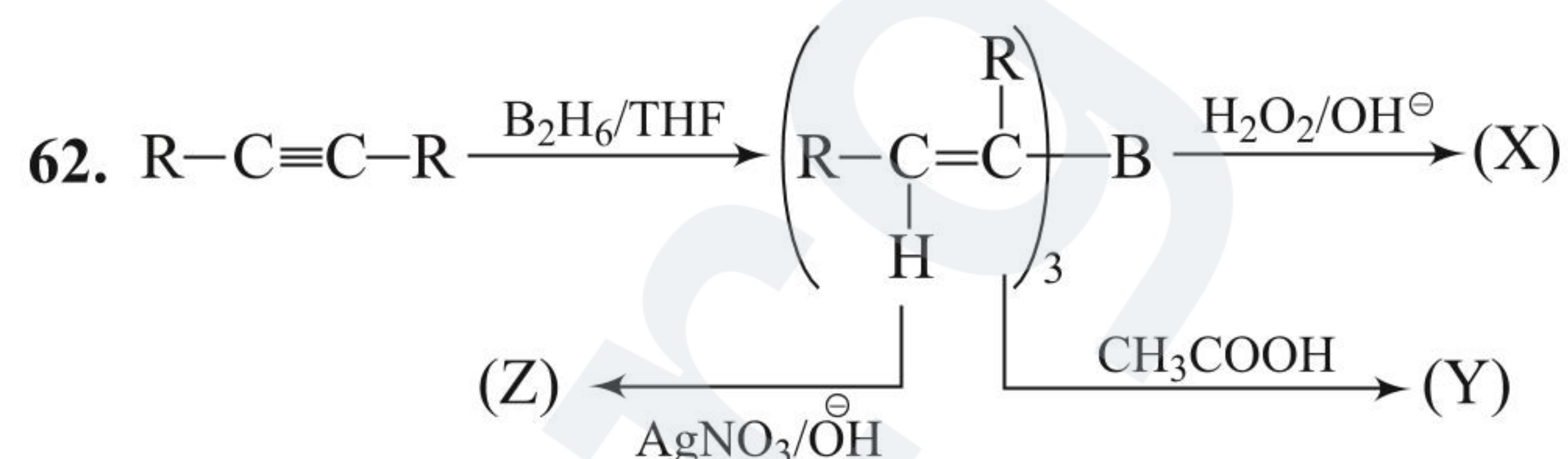
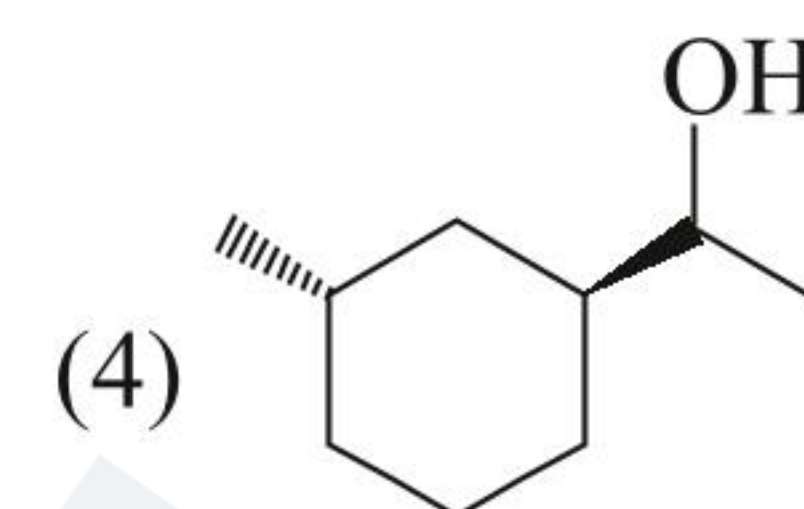
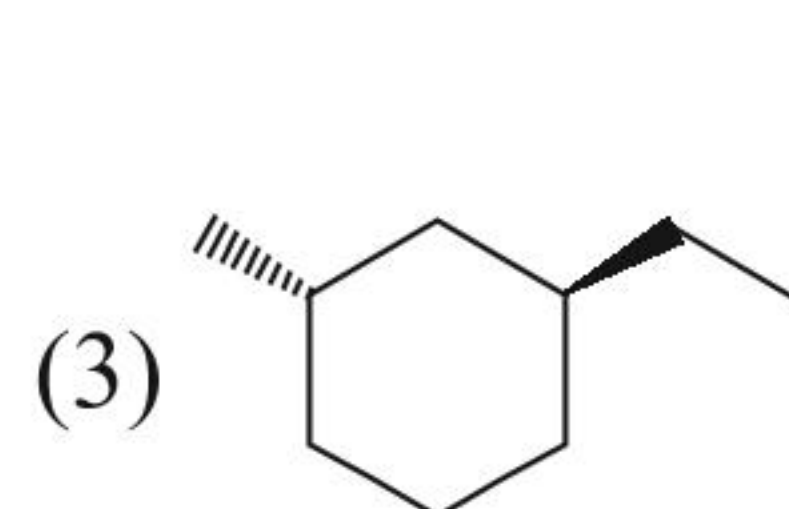
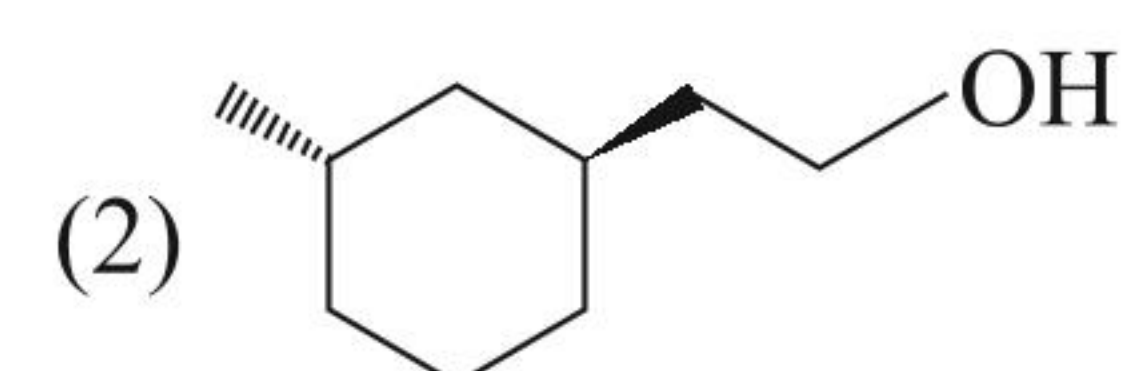
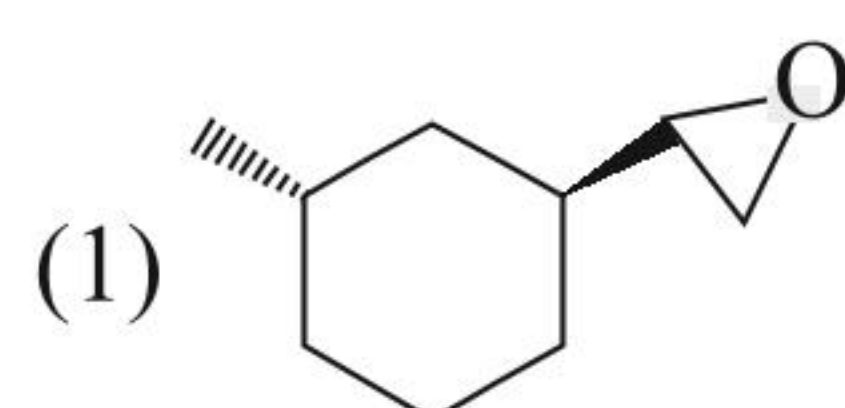
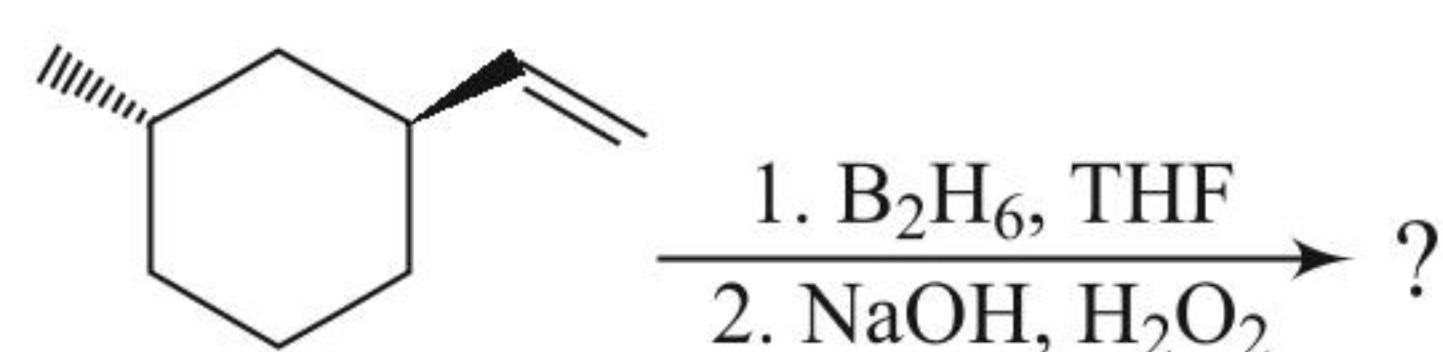
- (1) reduced from Cr^{6+} to Cr^{3+}
 (2) reduced from Cr^{3+} to Cr^{6+}
 (3) oxidised from Cr^{3+} to Cr^{6+}
 (4) oxidised from Cr^{6+} to Cr^{3+}



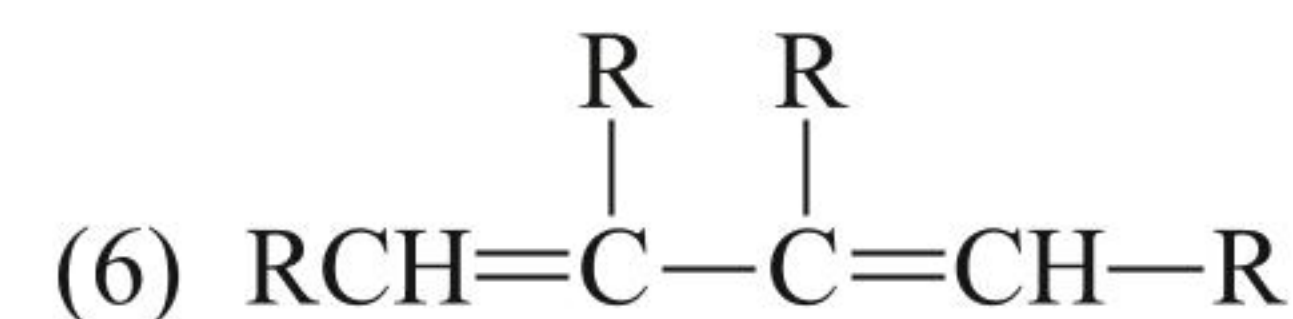
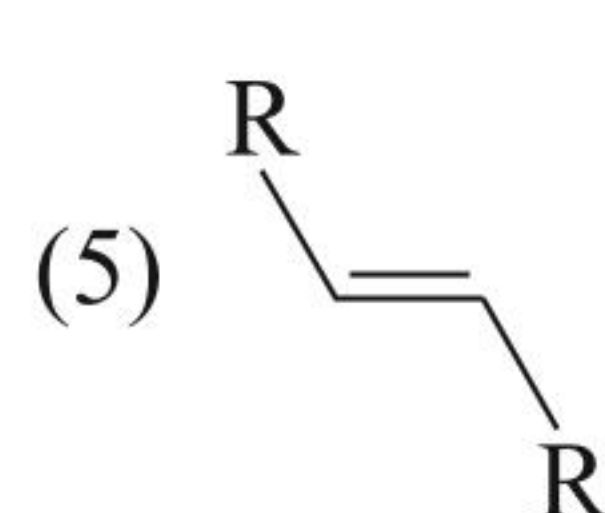
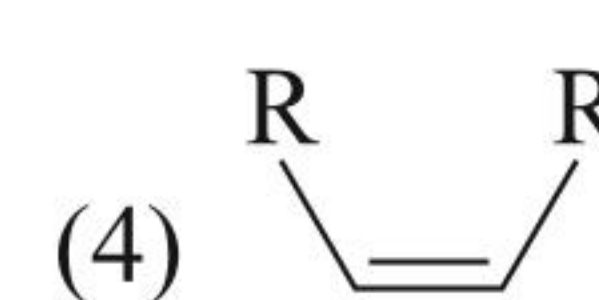
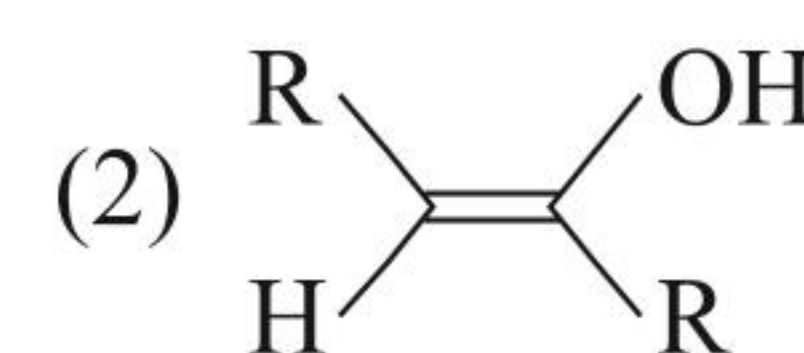
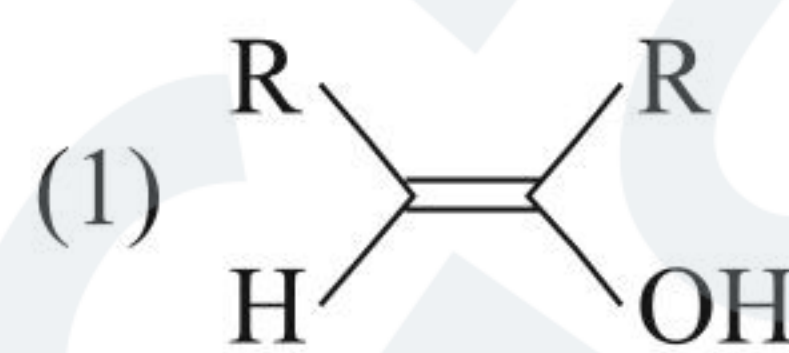
Product (C) is



61. What is the product of the following reactions?

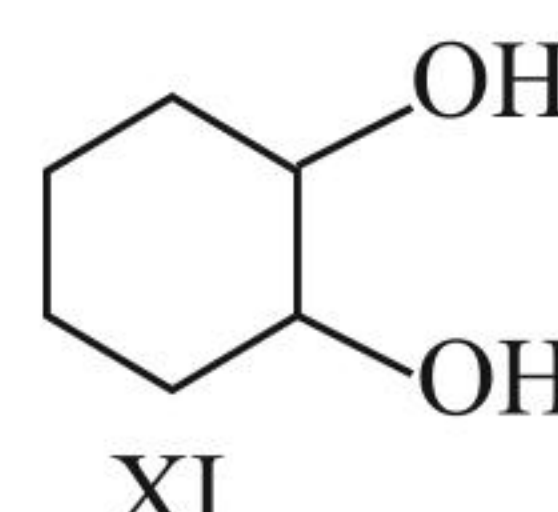
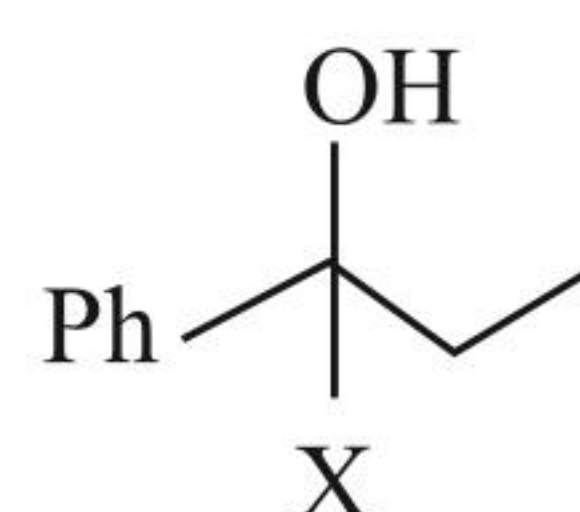
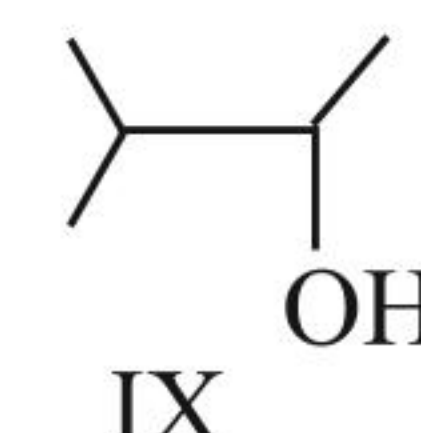
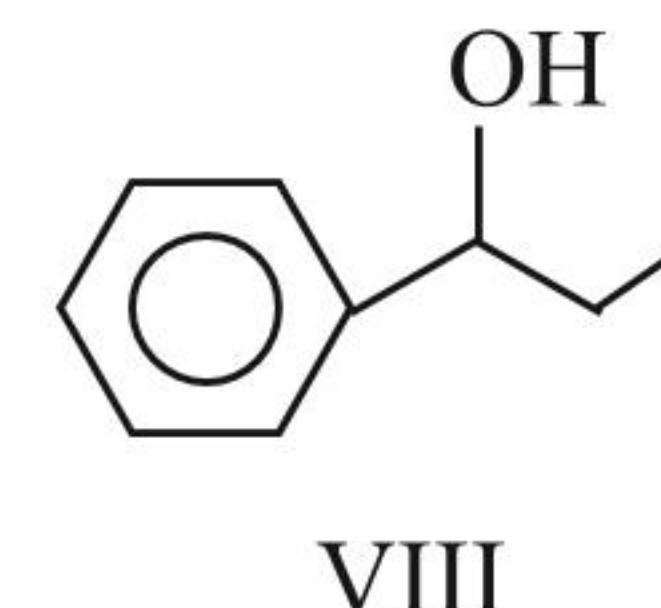
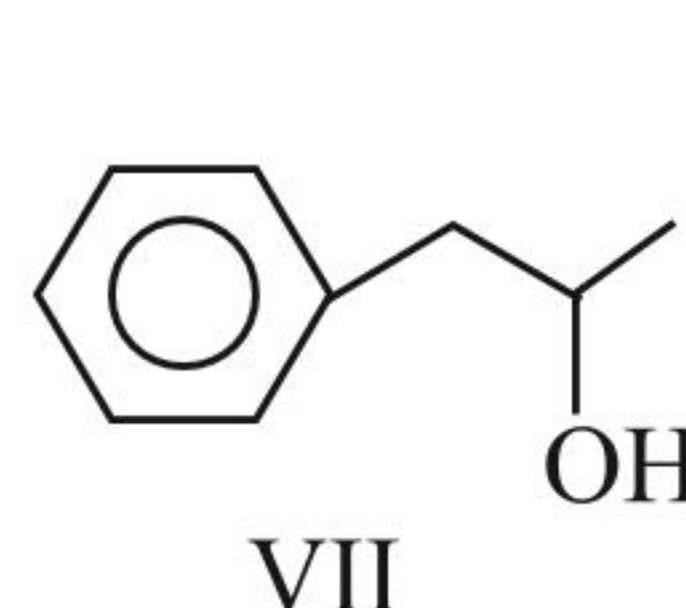
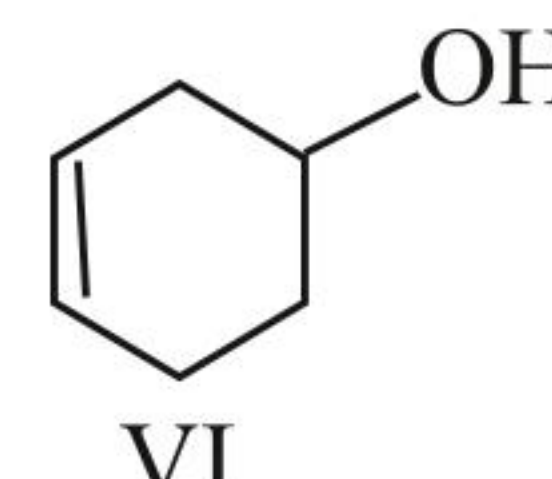
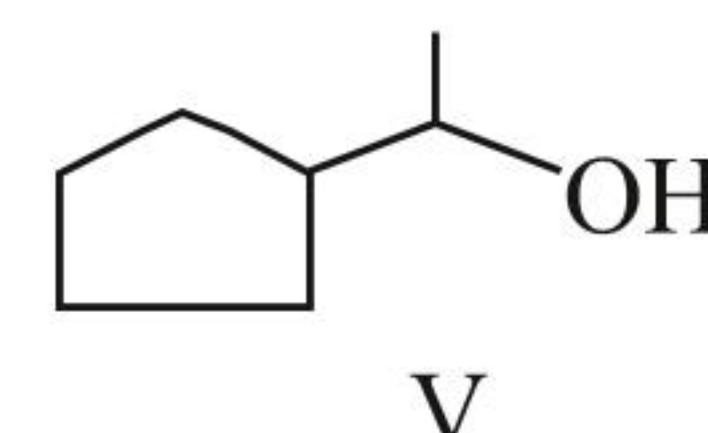
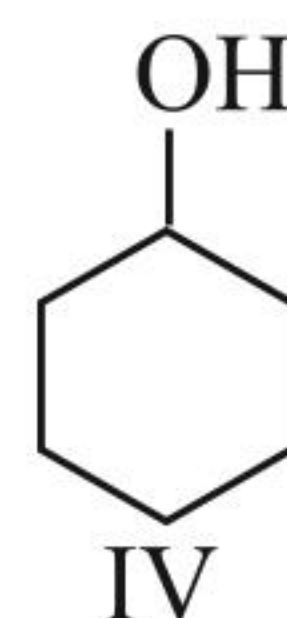
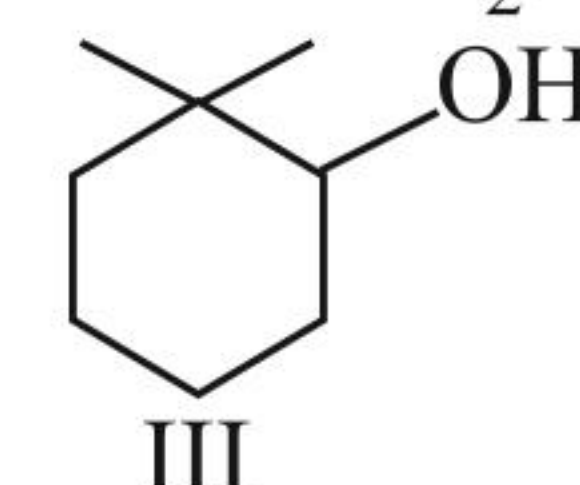
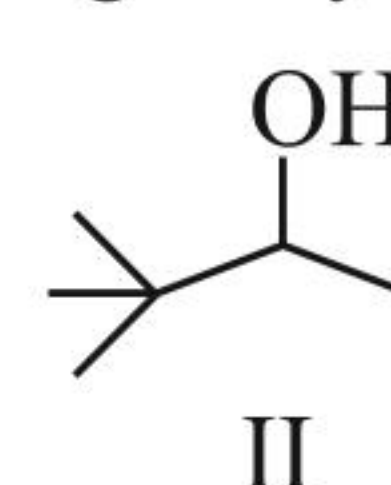
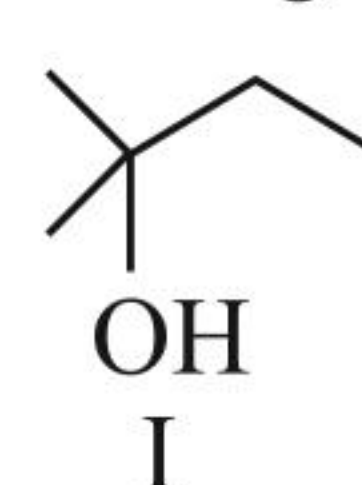


Amongst the following given compounds for (X), (Y) and (Z), which of the following is correct option.



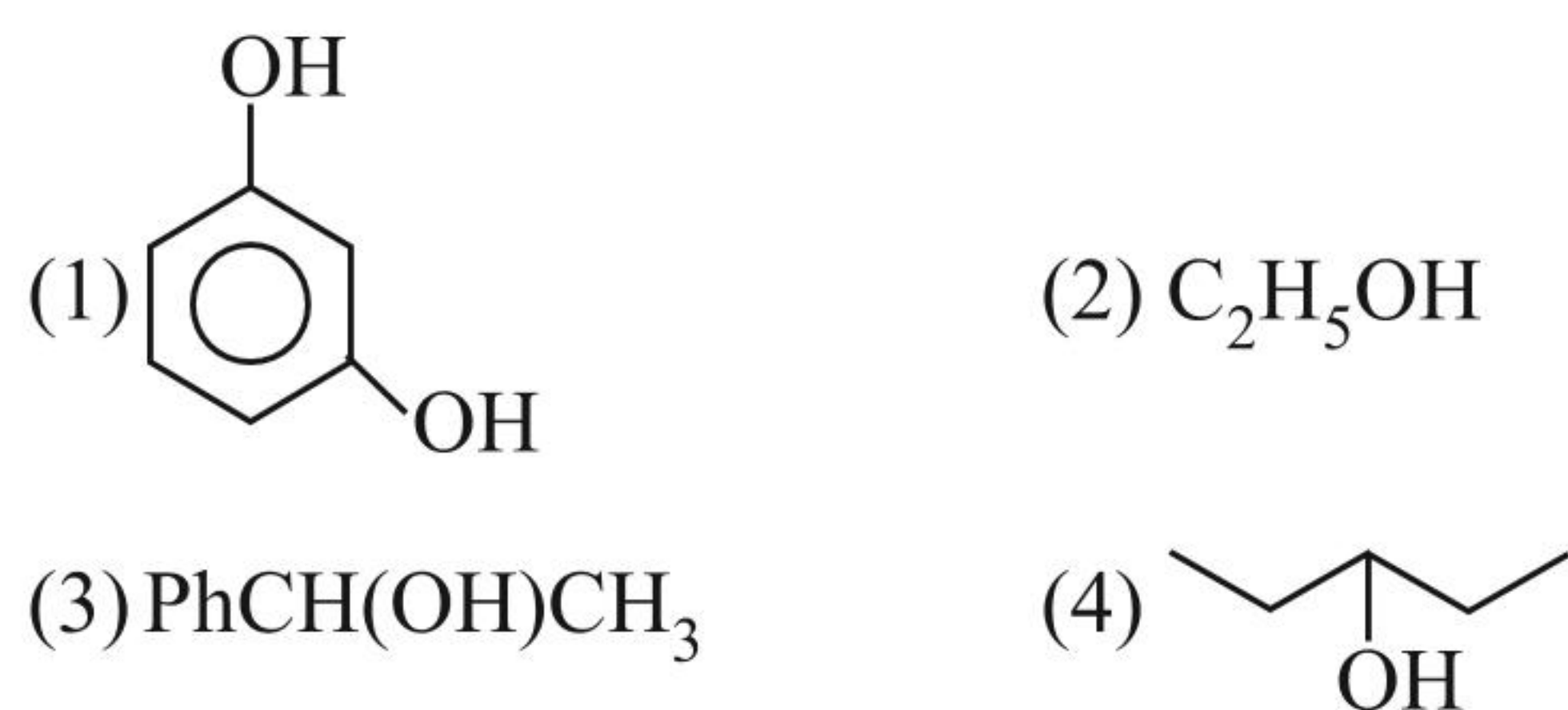
(X)	(Y)	(Z)
(1) (2)	(4)	(5)
(2) (1)	(5)	(4)
(3) (3)	(4)	(6)
(4) (3)	(5)	(6)

63. Out of the following alcohols, how many of them will show rearrangement during dehydration with conc. H_2SO_4 .

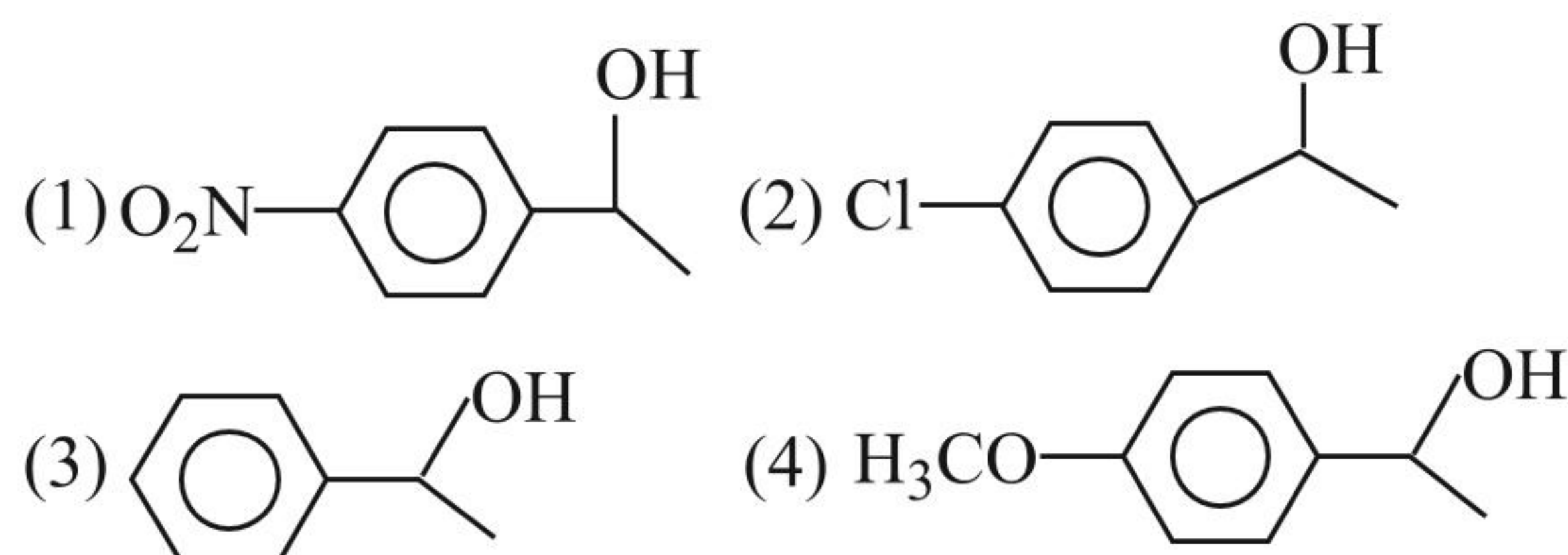


- (1) 7 (2) 6
(3) 5 (4) 4

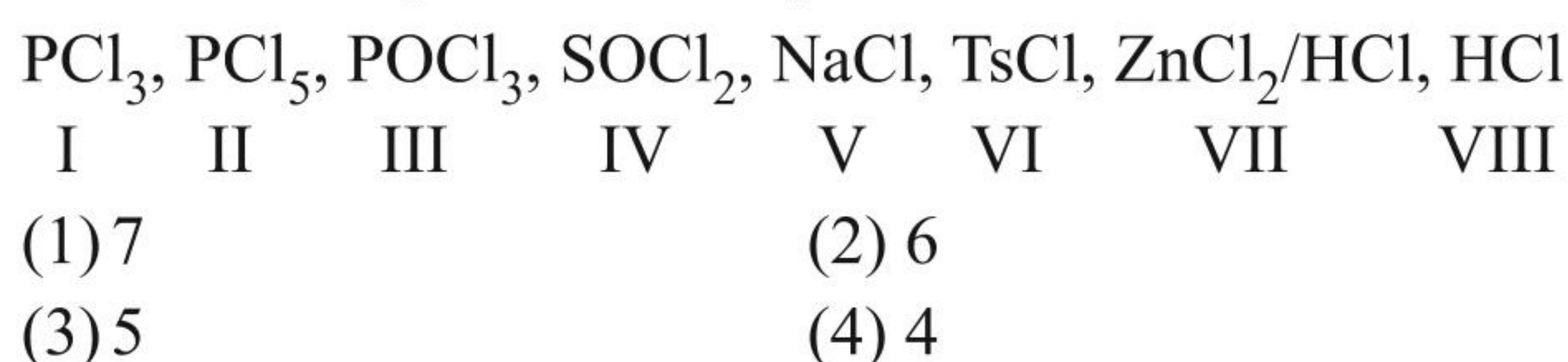
64. Which of the following does not give iodoform test?



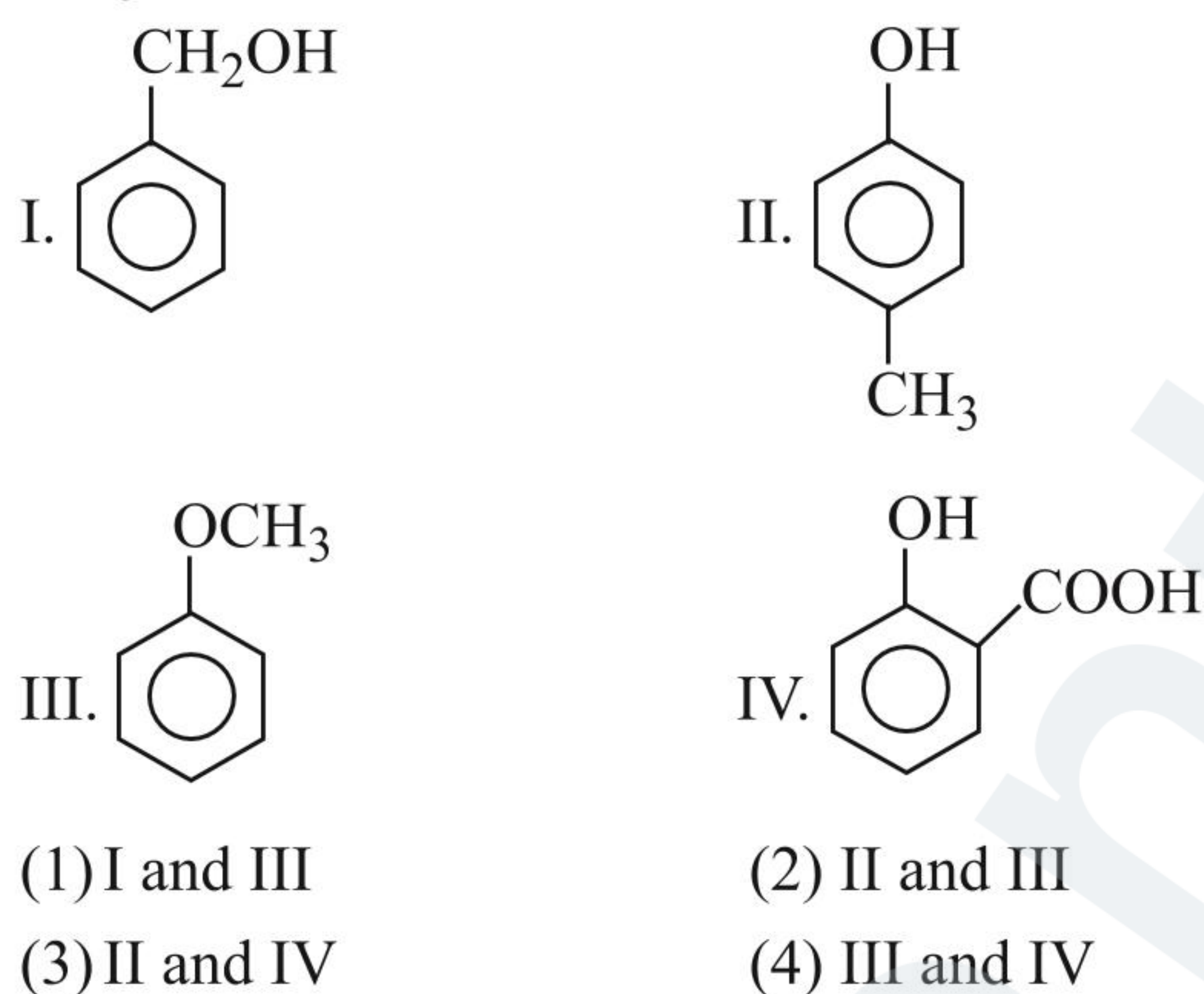
65. Which of the following will undergo easiest dehydration?



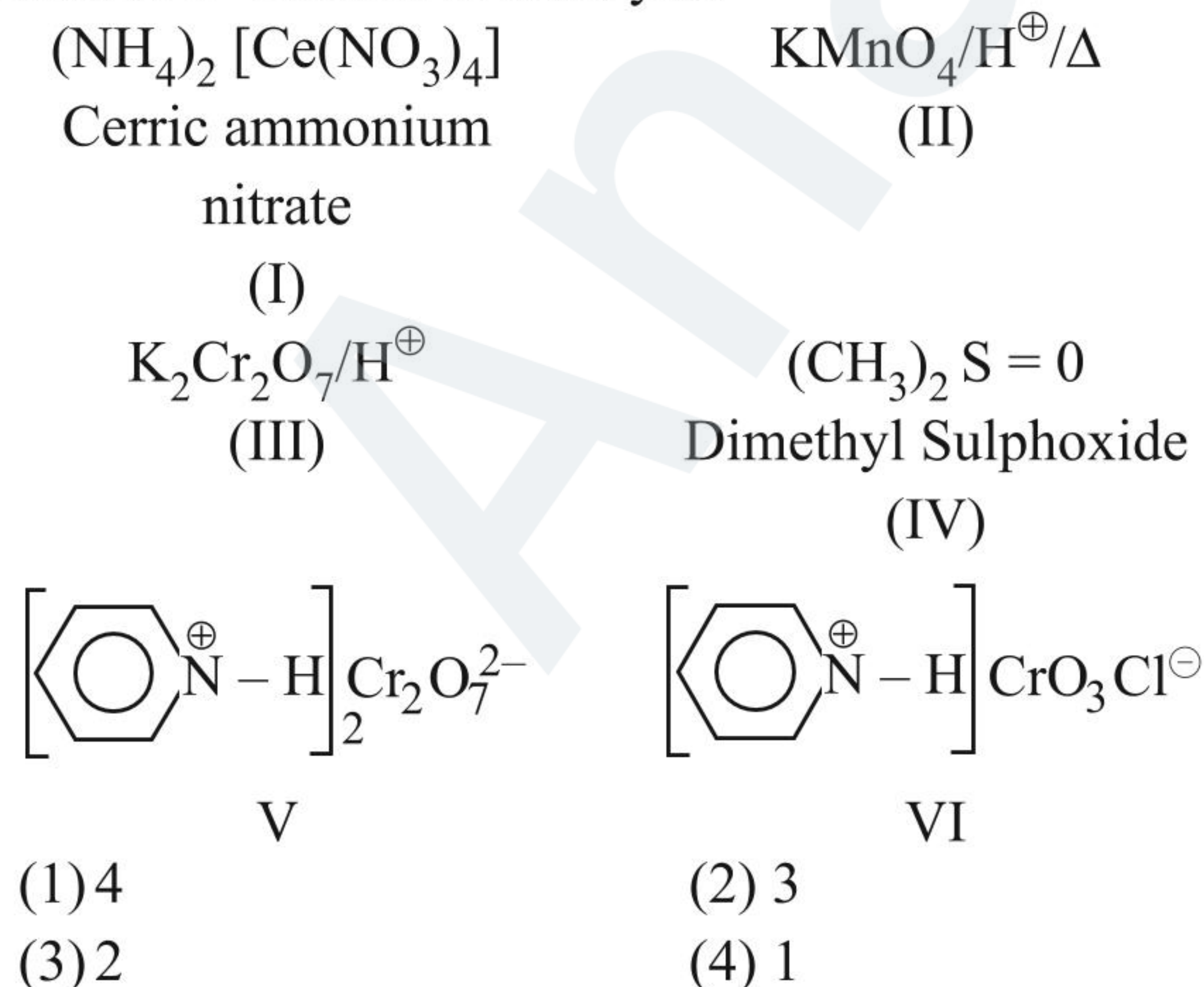
66. Out of the following reagents, how many reagents can convert (RCH_2OH to RCH_2Cl).



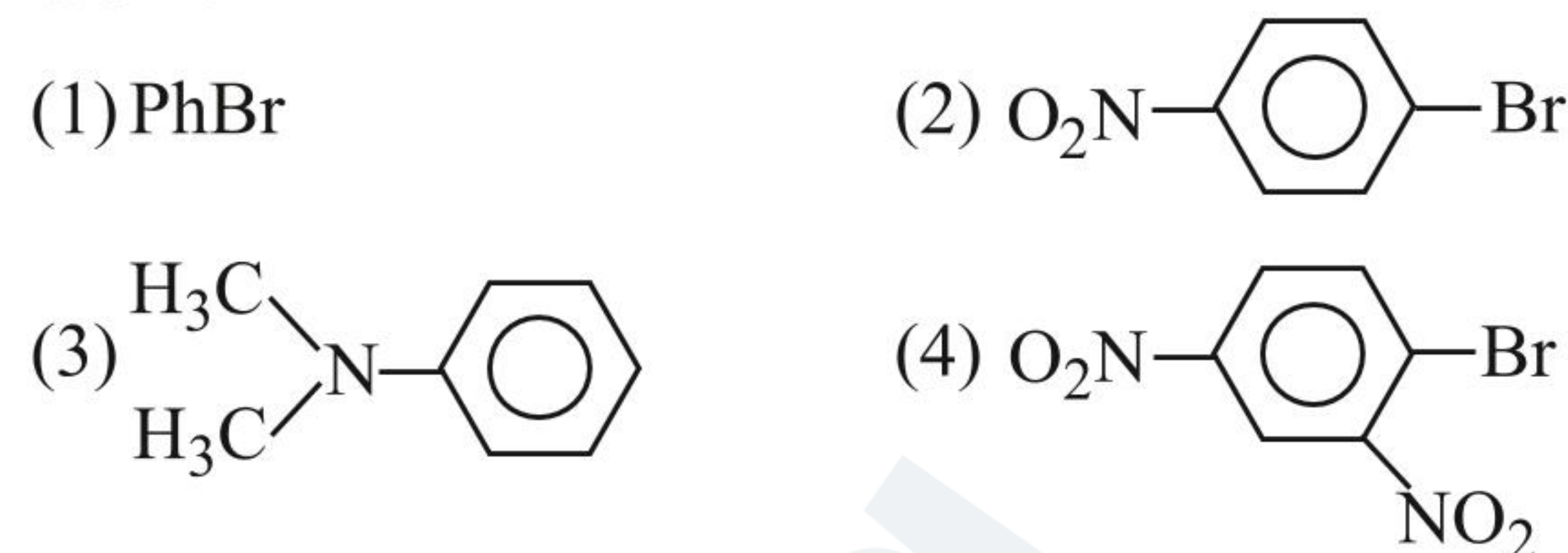
67. Which of the following give purple colour with neutral $FeCl_3$?



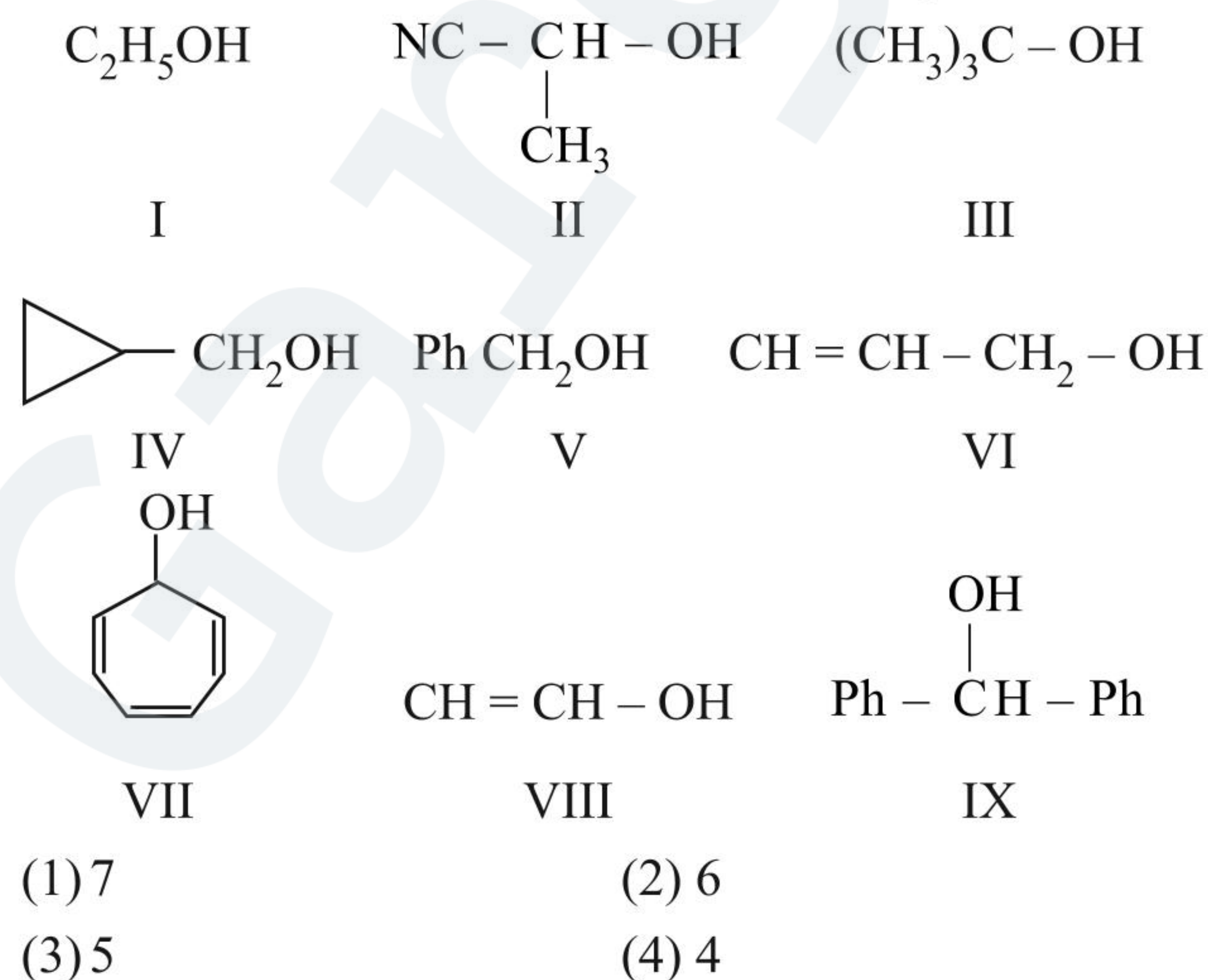
68. Out of the following reagents, how many reagents will convert 1° alcohol to aldehyde.



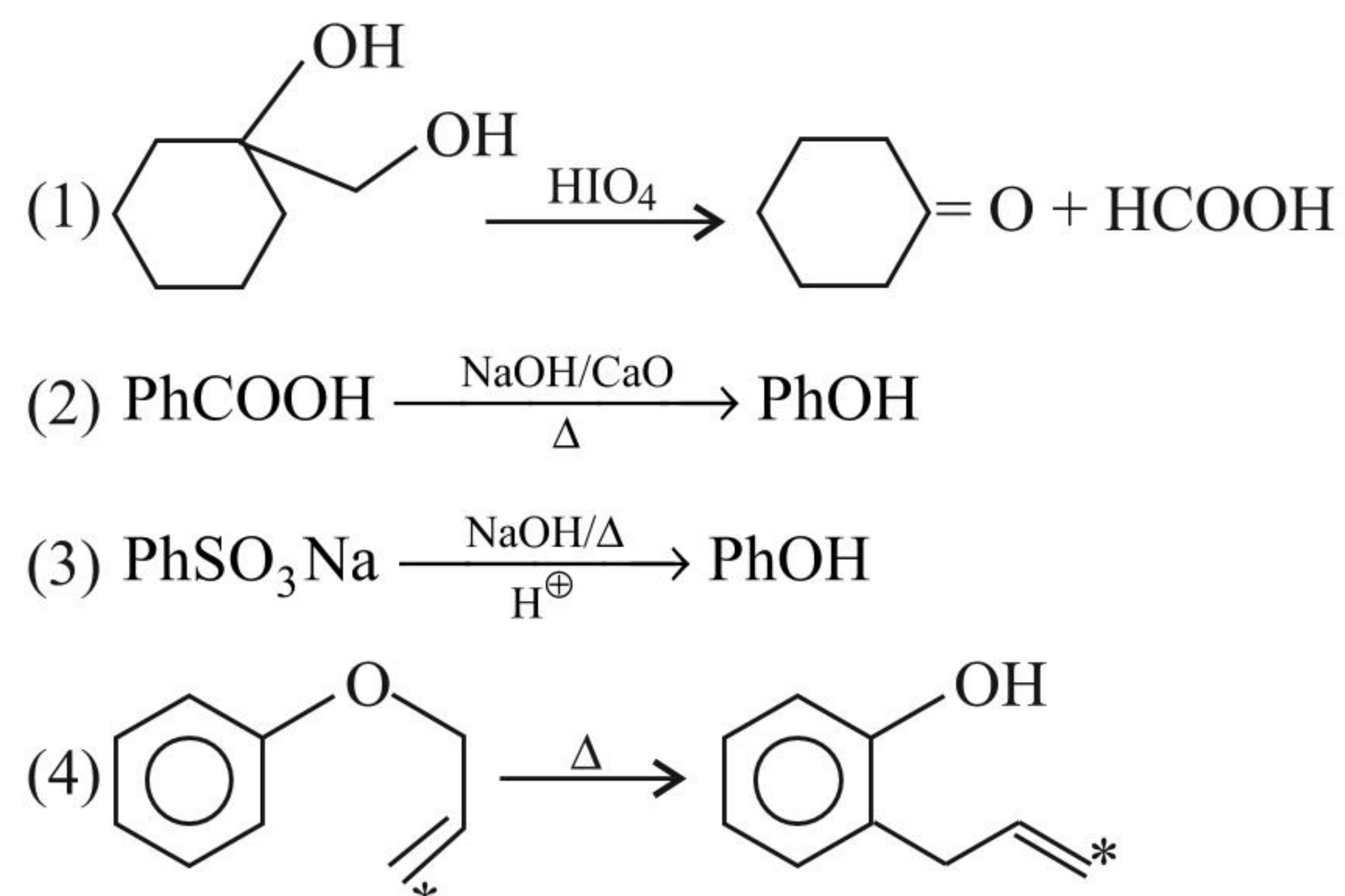
69. Which of the following will react most readily with aqueous $NaOH$?



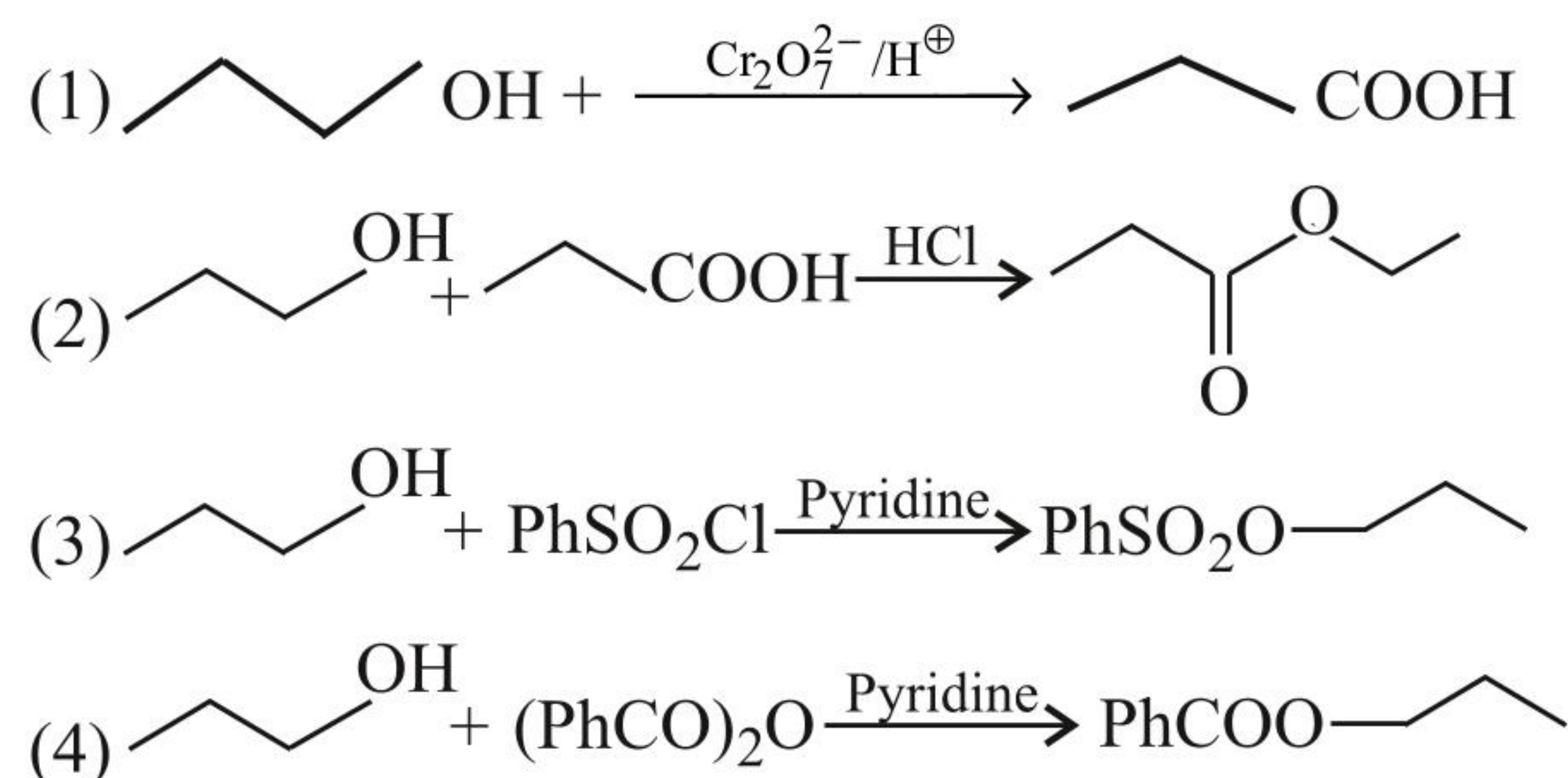
70. Out of the following compounds, how many compounds give white turbidity on treatment with $ZnCl_2/HCl$?



71. Select correct statement.

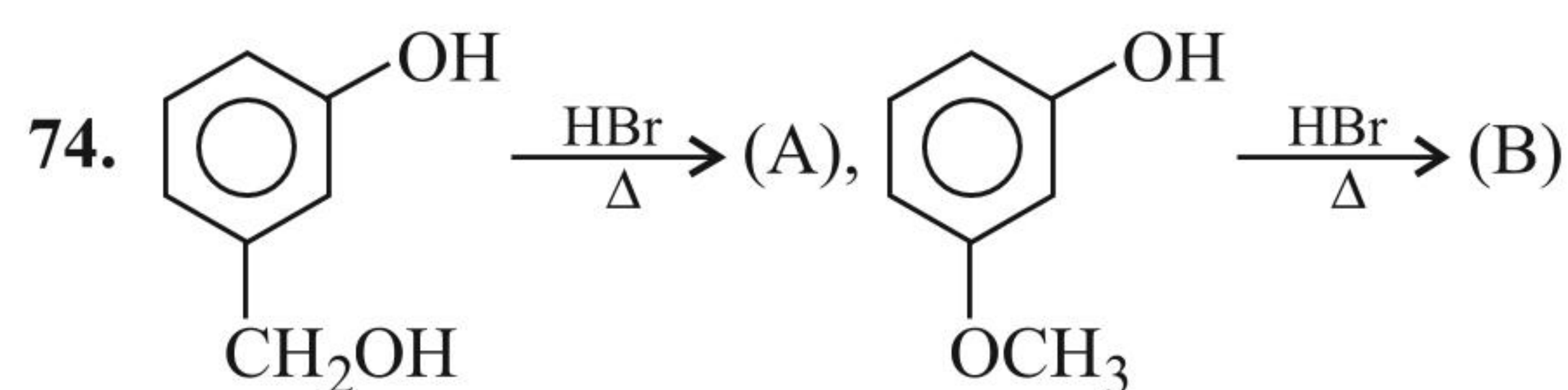


72. Select the incorrect reaction:

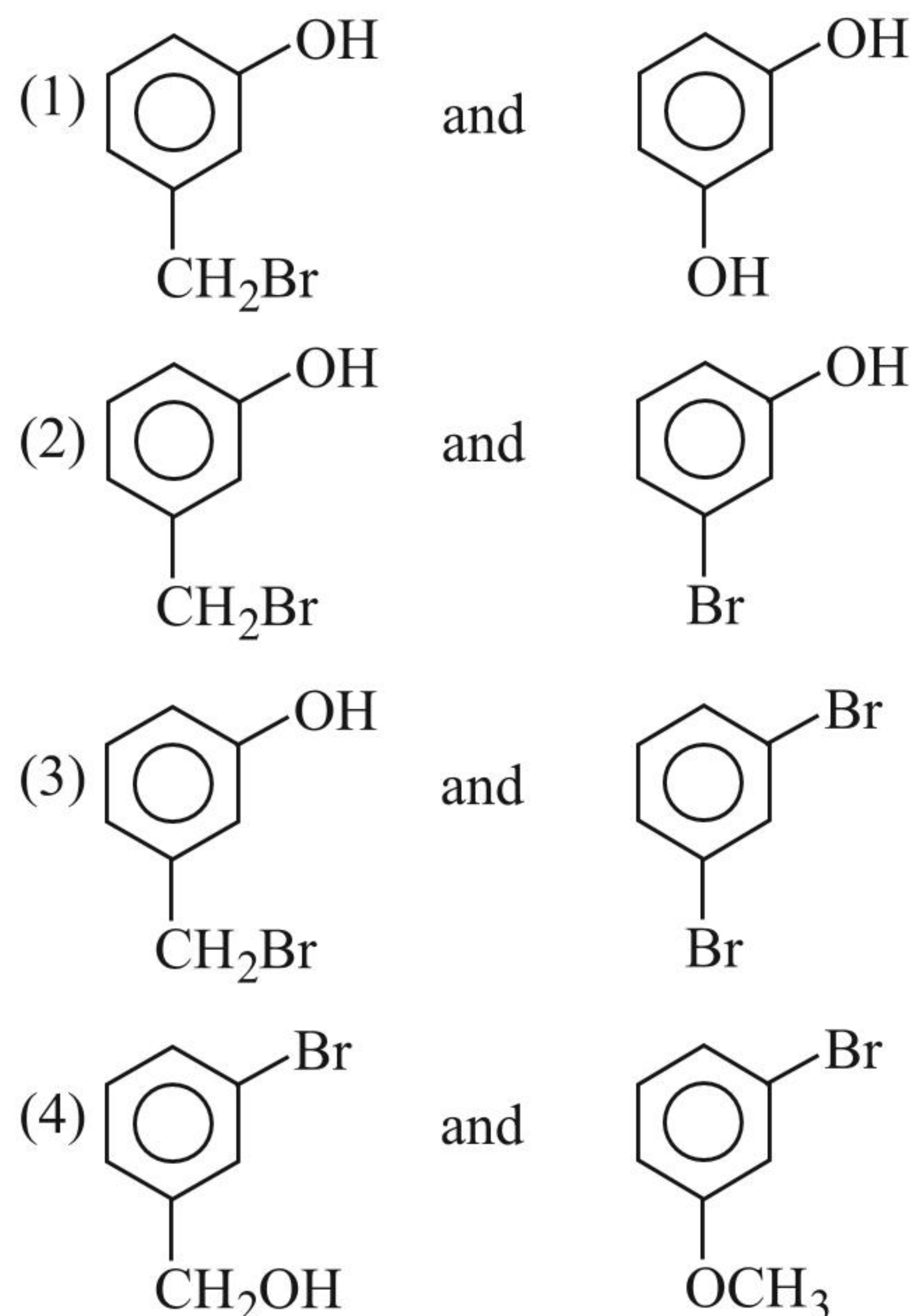


73. In the Liebermann nitroso reaction, changes in the colour of phenol occur as:

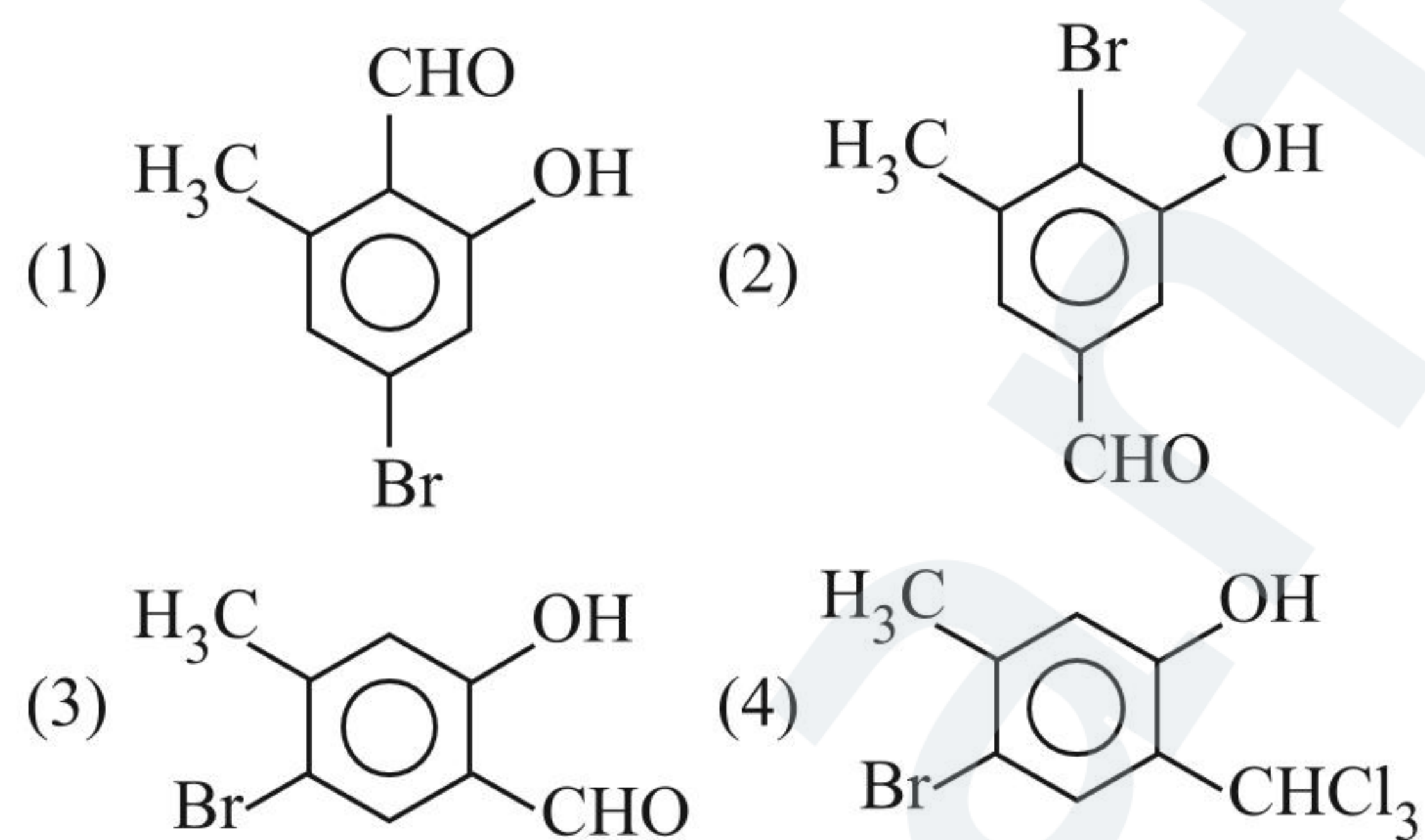
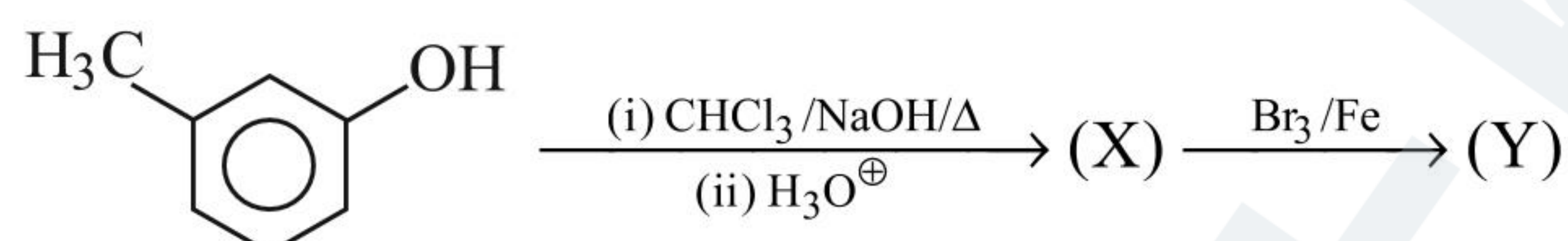
- (1) Red \rightarrow brown \rightarrow white
 (2) White \rightarrow red \rightarrow green
 (3) Red \rightarrow green \rightarrow deep blue
 (4) Brown or red \rightarrow deep blue \rightarrow deep green



The product (A) and (B) are respectively:



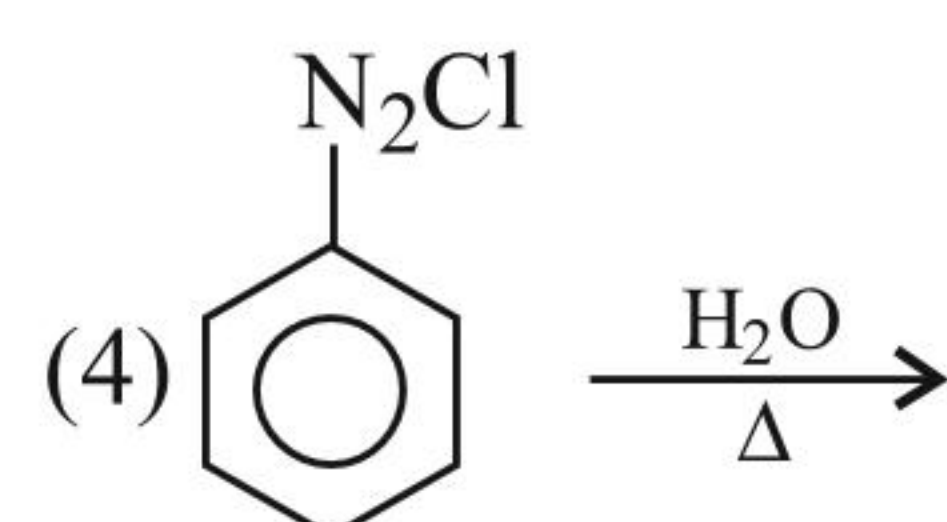
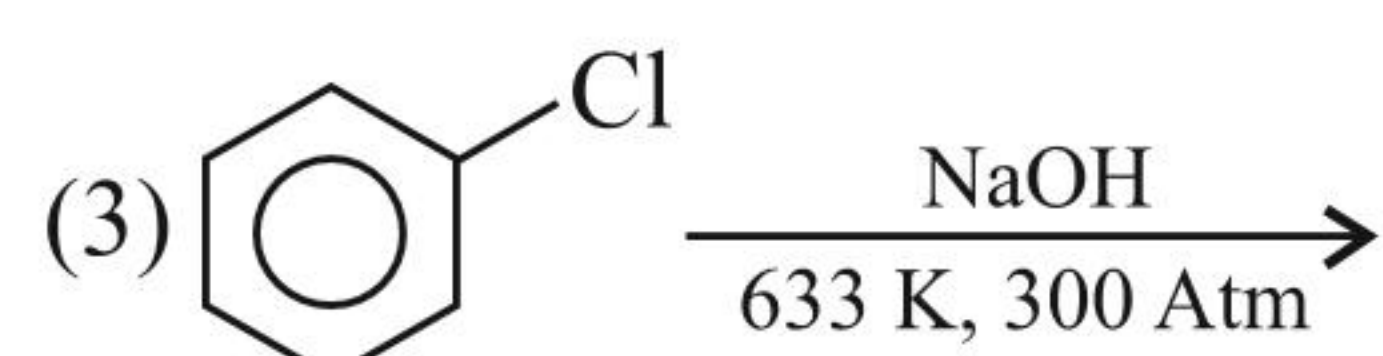
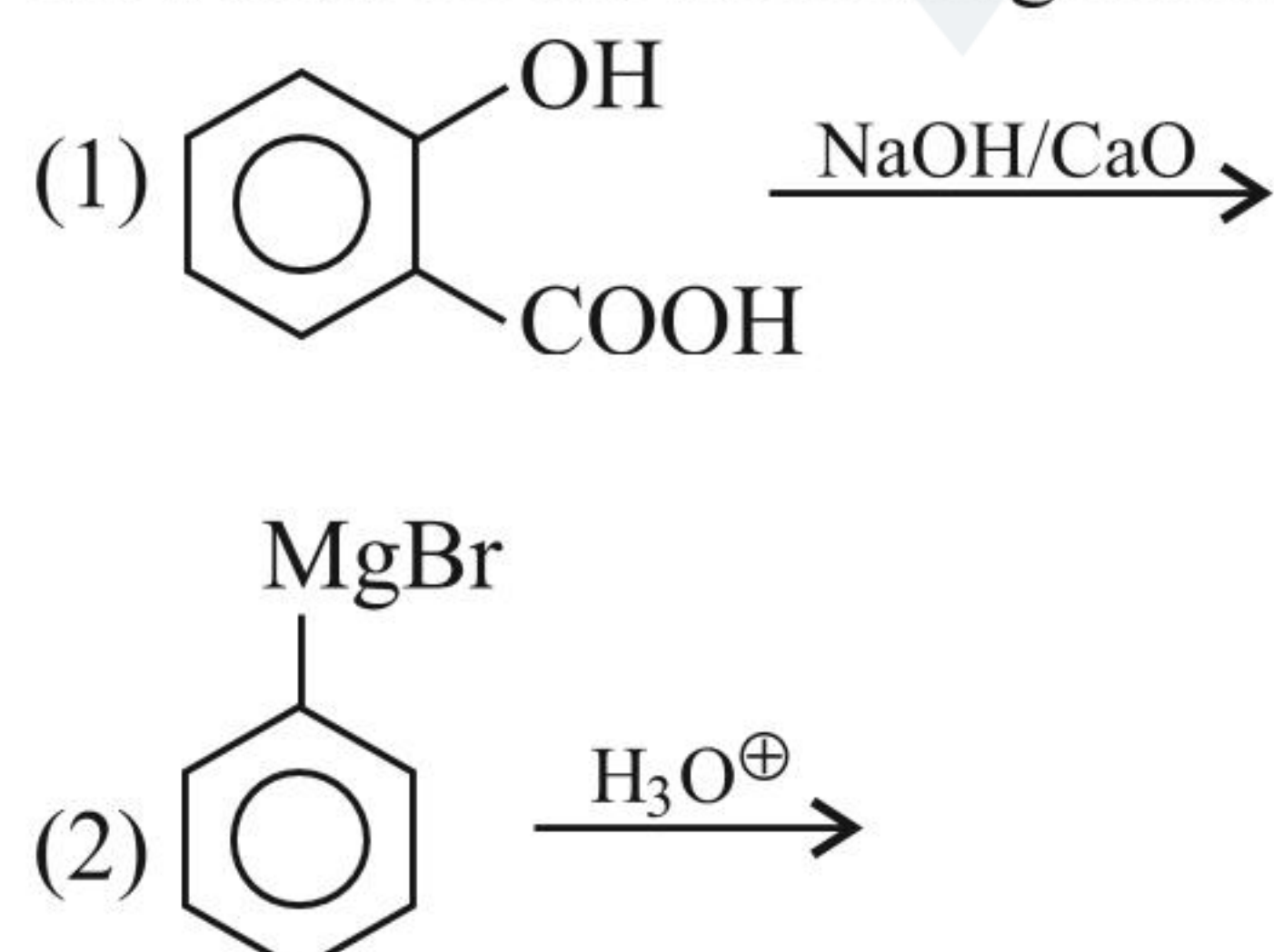
75. The product (Y) of the following sequence of reactions would be:



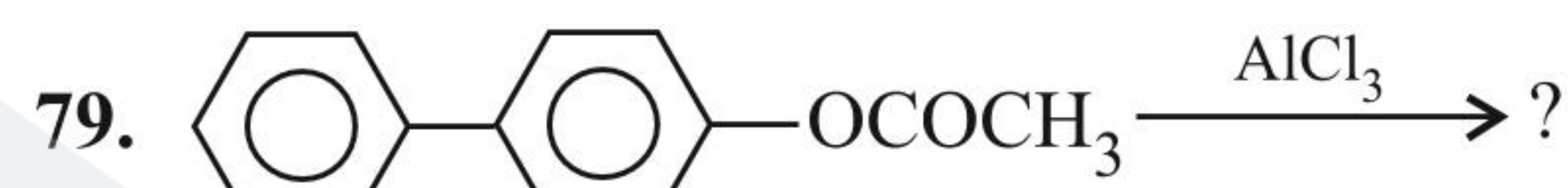
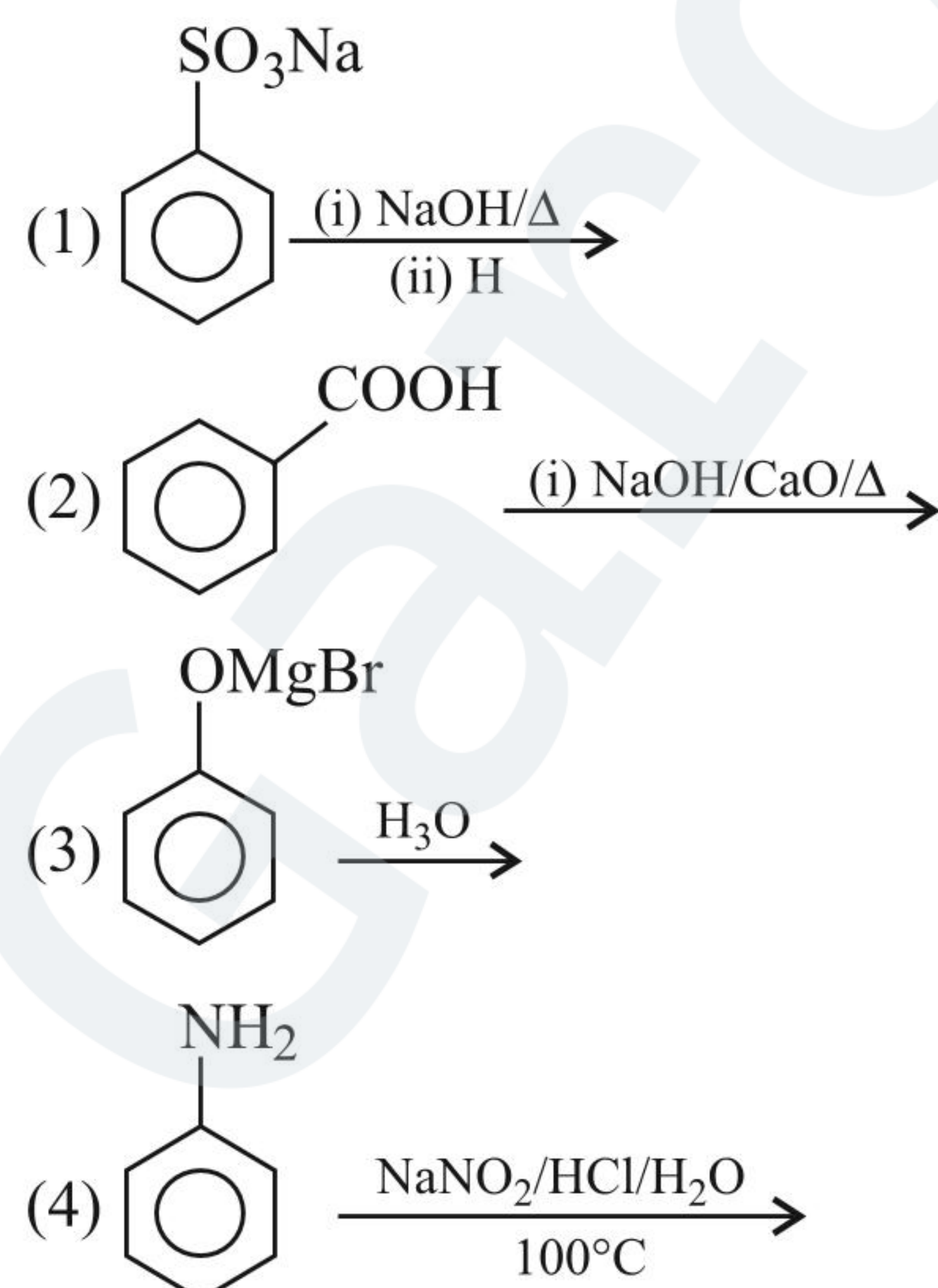
76. Which of the following pair of compounds can be separated by aq. NaHCO_3 ?

- (1) Phenol and benzyl alcohol
 (2) Benzoic acid and Picric acid
 (3) *p*-Nitrophenol and *p*-Methoxyphenol
 (4) Resorcinol and *o*-Cresol

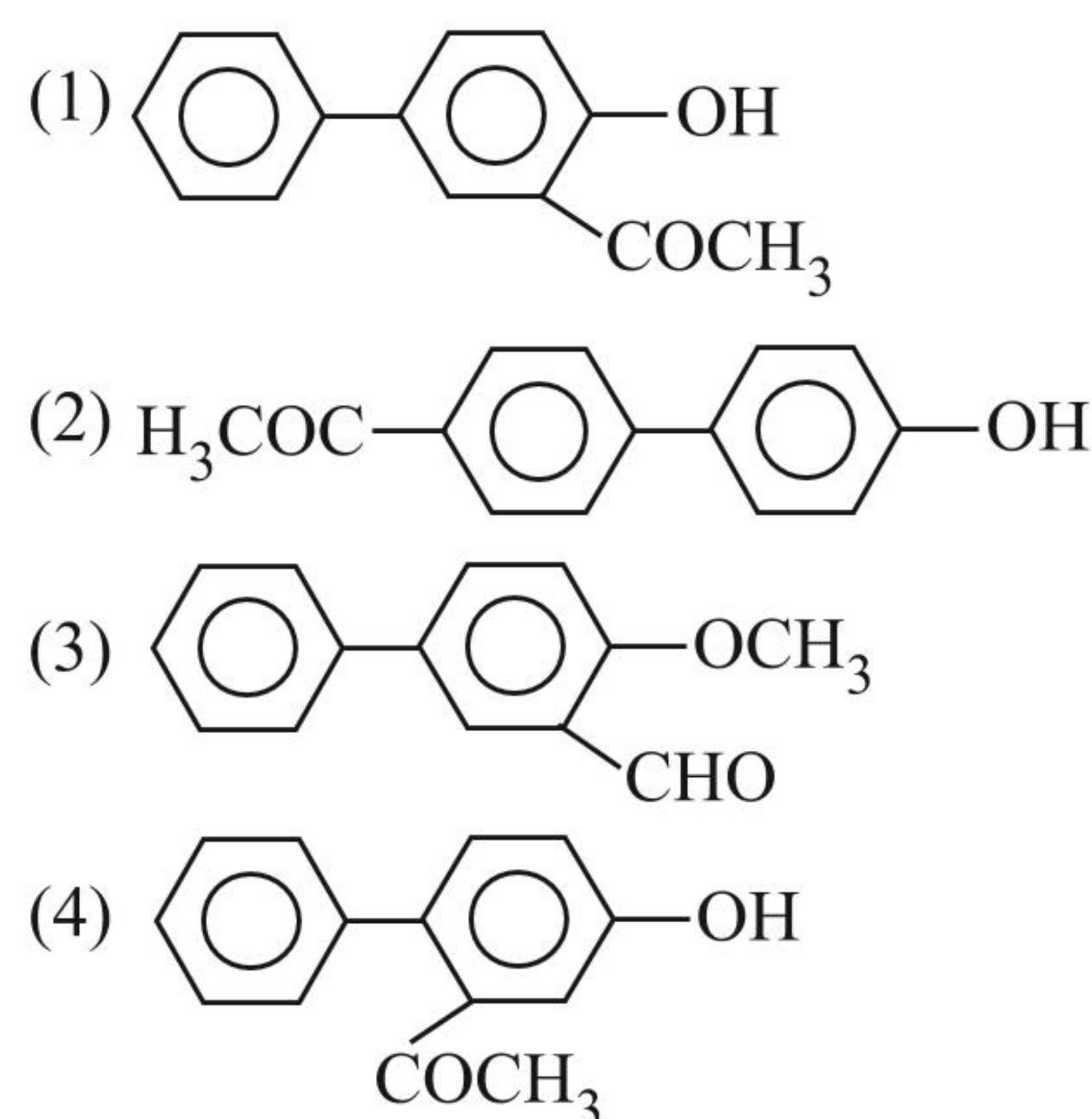
77. In which of the following reactions phenol is not obtained?



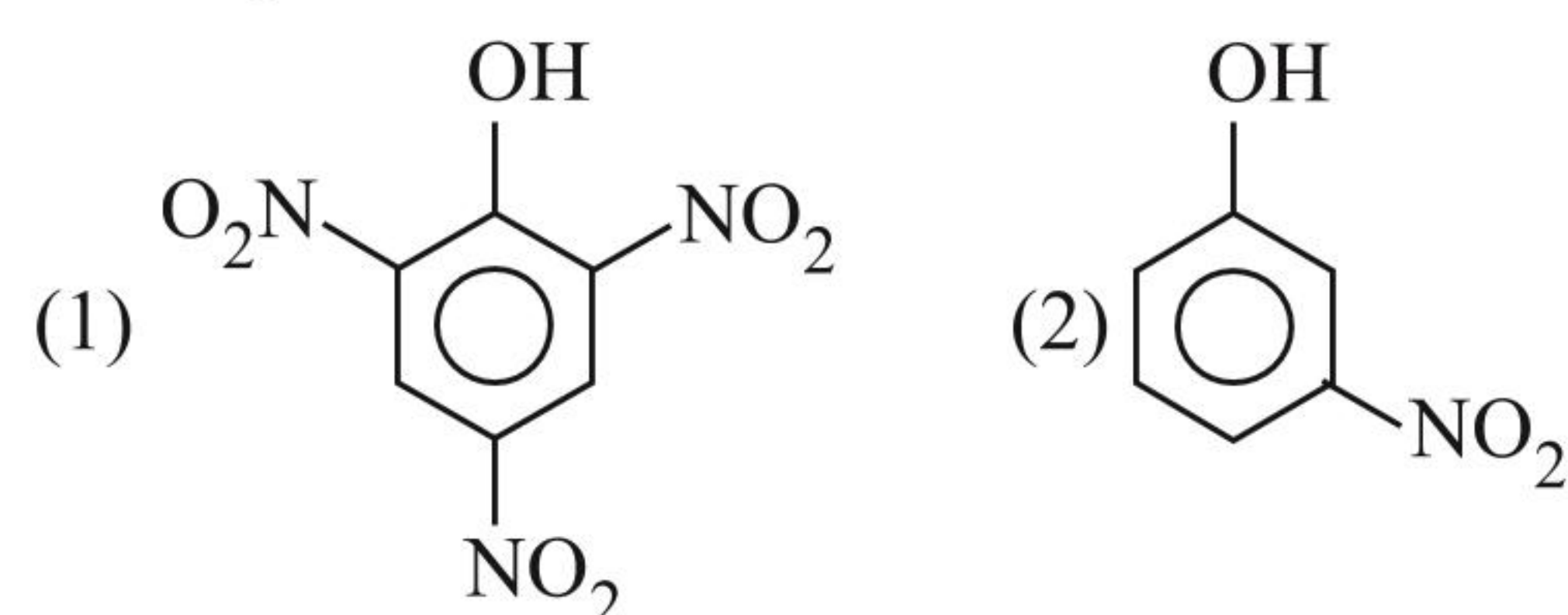
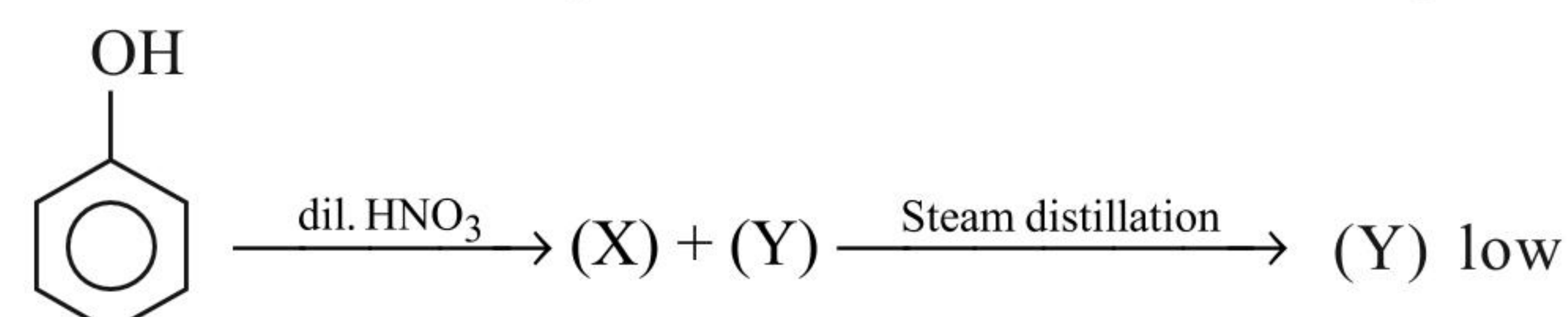
78. Phenol is not obtained by:

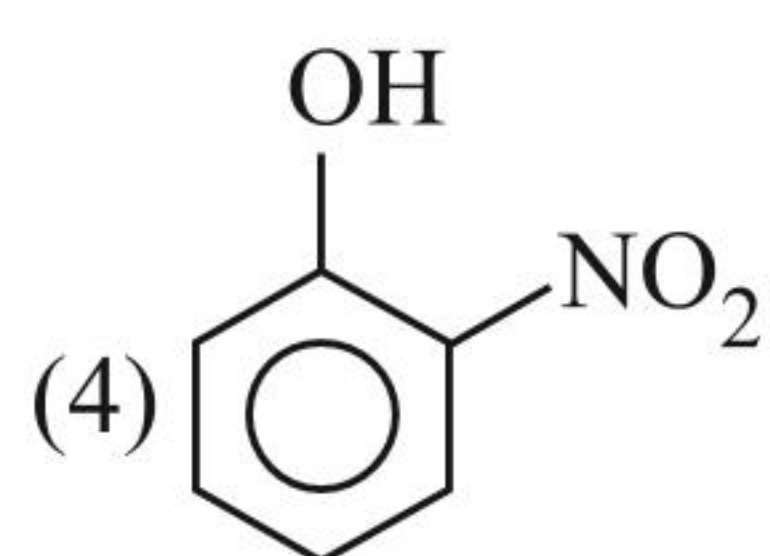
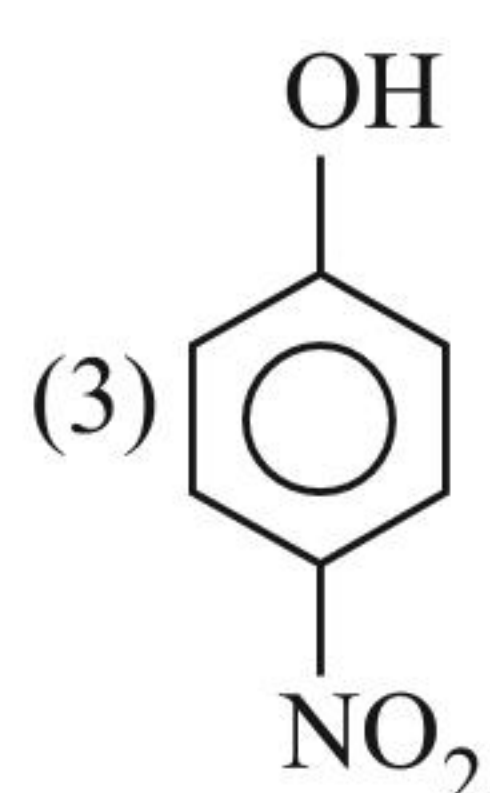


Major product is:

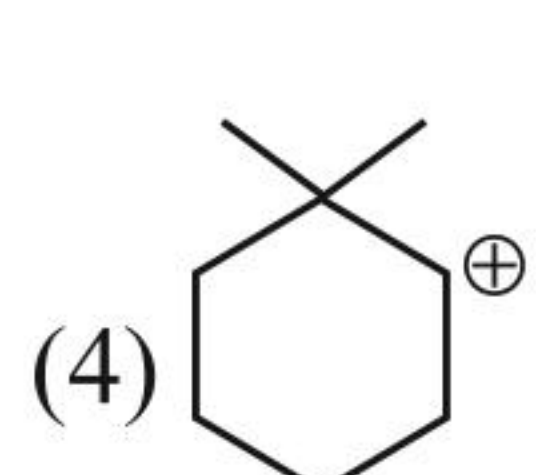
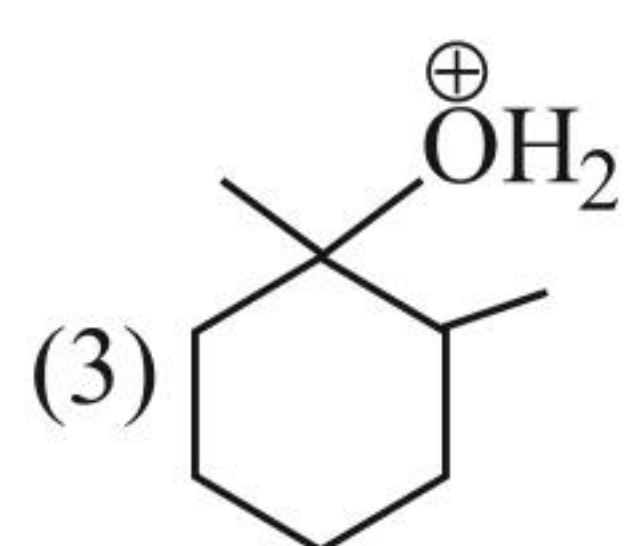
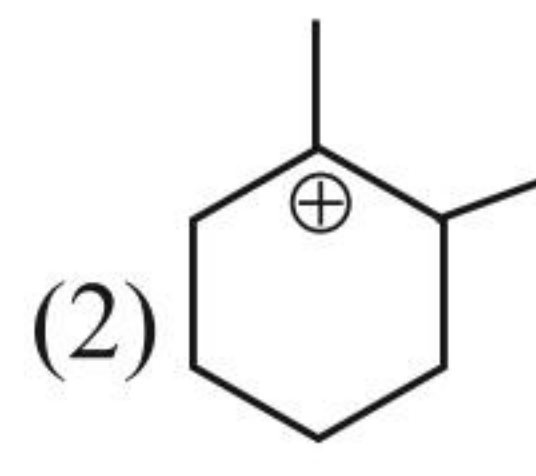
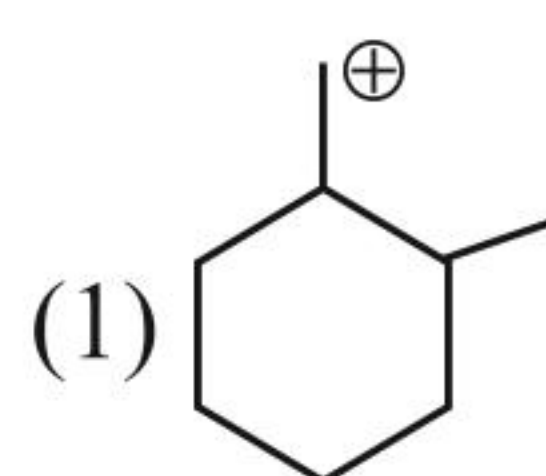
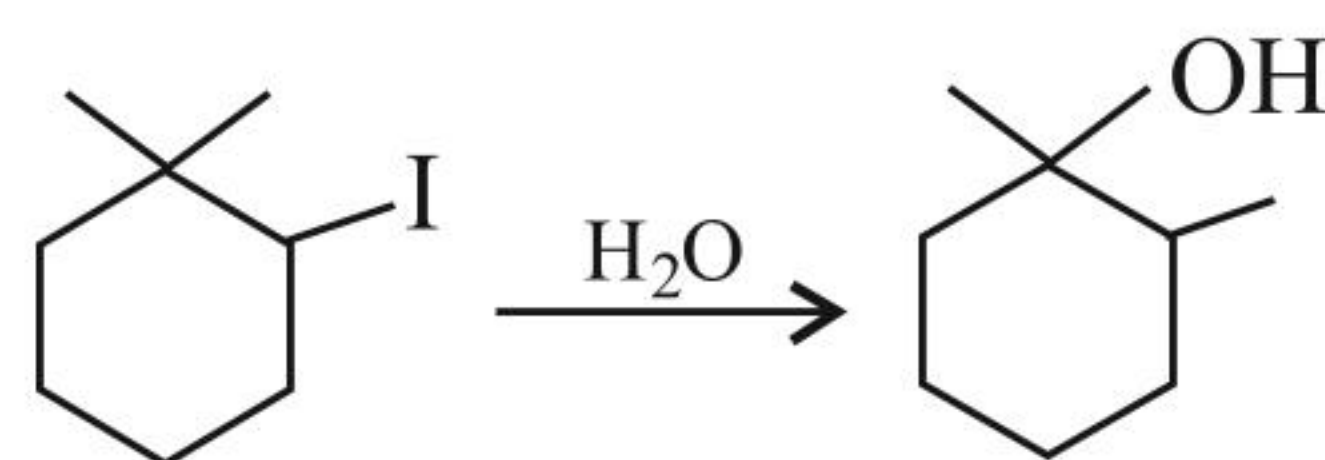


80. Observe the following reaction, and select the correct option.





81. Which of the following is not expected to be intermediate of the following reaction?



82. Among the following the number of alcohols showing iodoform test is:

- (a) CH_3OH , (b) $\text{CH}_3\text{CH}_2\text{OH}$, (c) $(\text{CH}_3)_2\text{CHOH}$,
(d) $(\text{CH}_3)_3\text{C-OH}$, (e) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, (f) $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$, (g) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, (h) $(\text{C}_2\text{H}_5)_2\text{CHOH}$, (i) $\text{CH}_3\text{CHOHCH}(\text{CH}_3)_2$

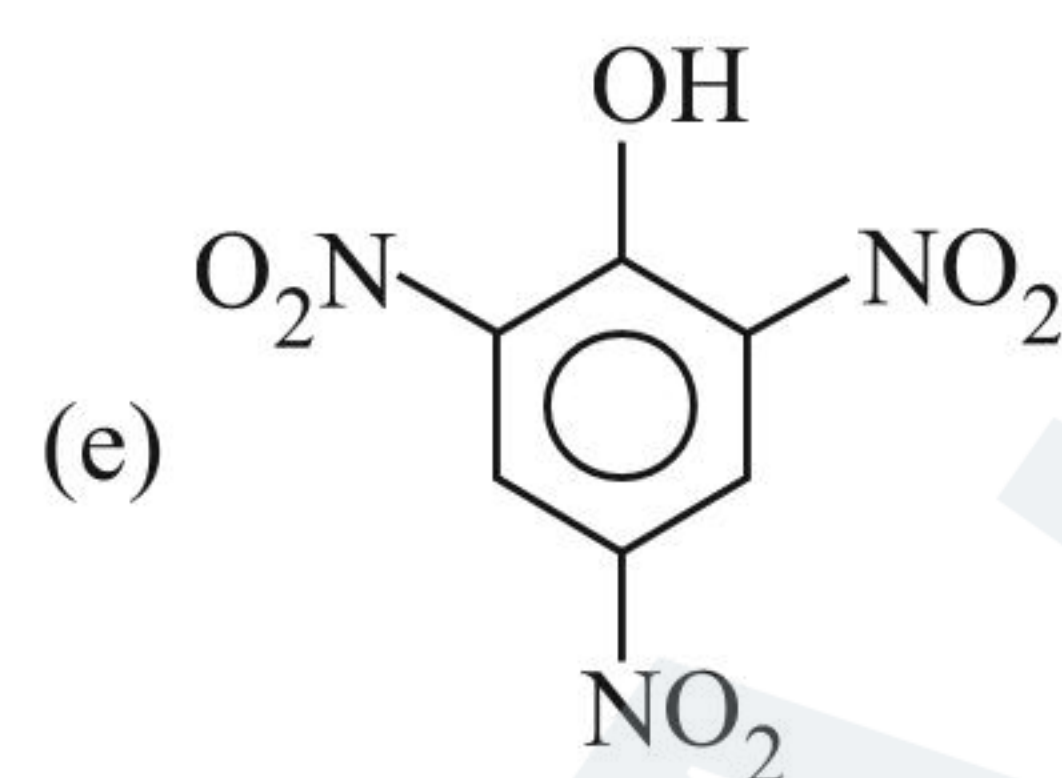
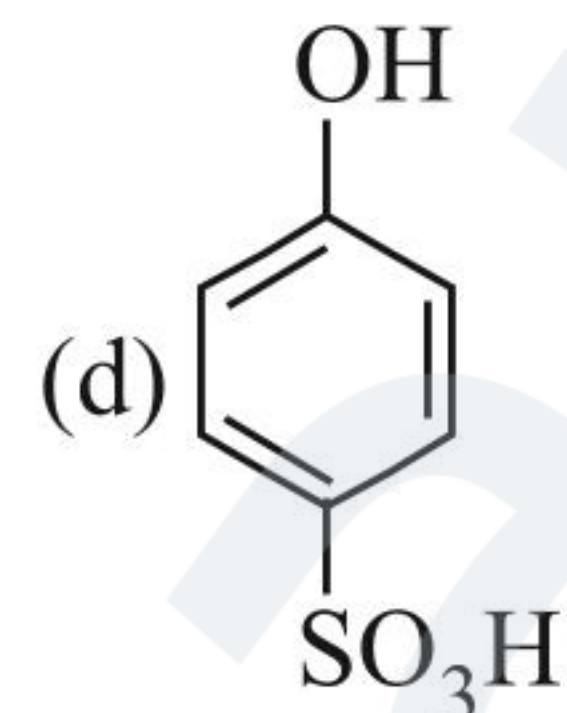
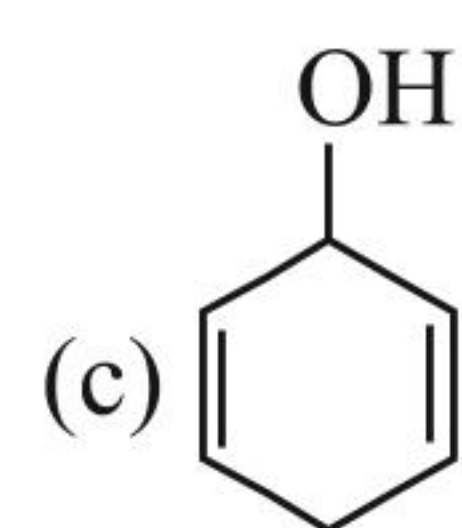
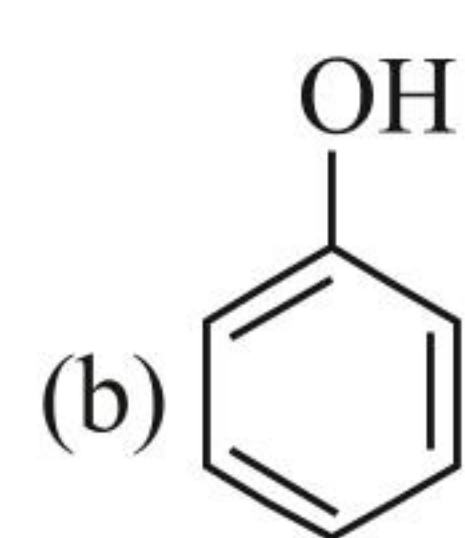
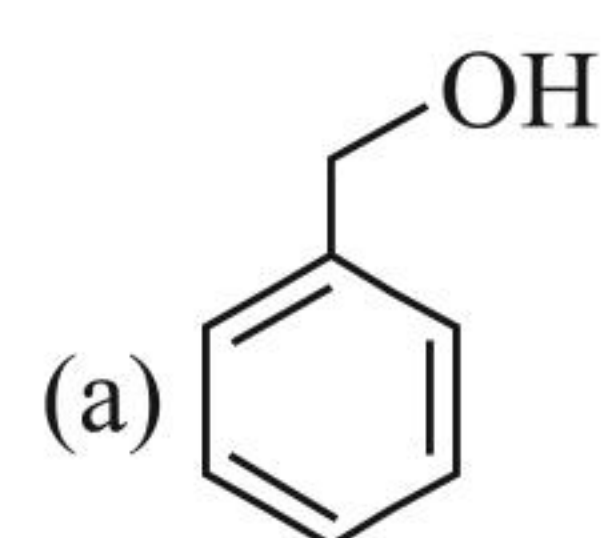
(1) 4

(2) 5

(3) 6

(4) 7

83. How many compounds will decolorise $\text{Br}_2/\text{H}_2\text{O}$?



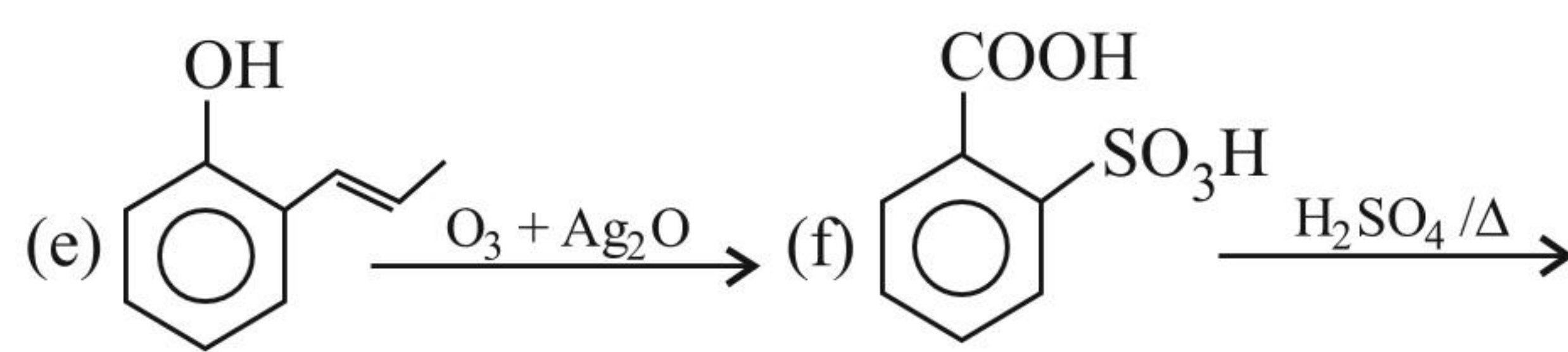
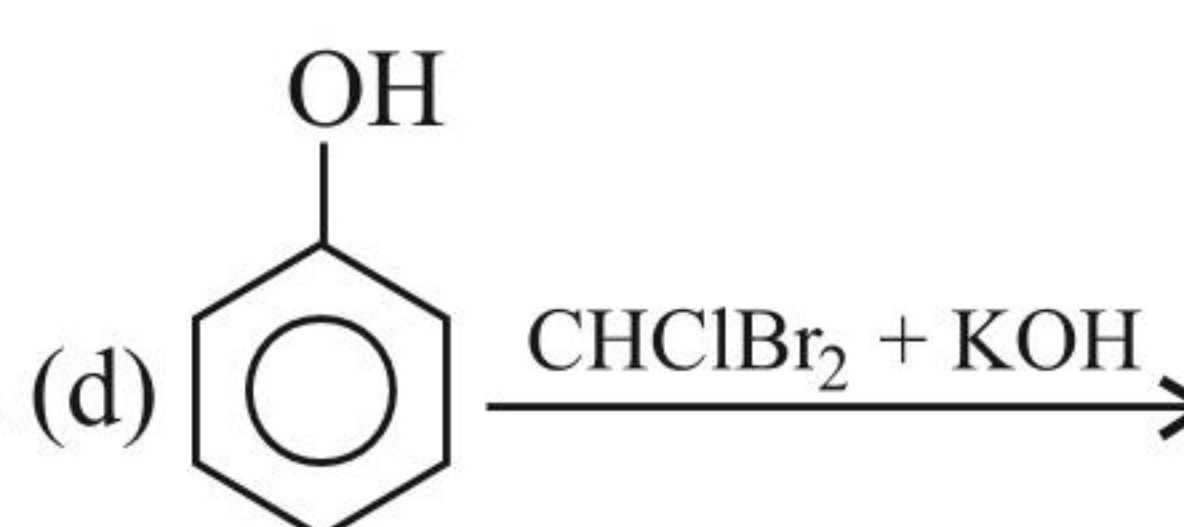
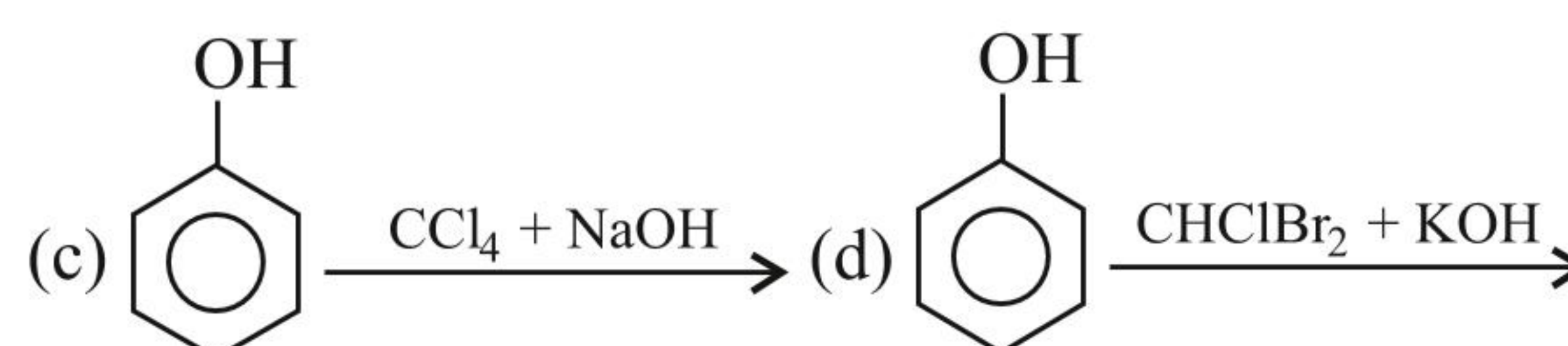
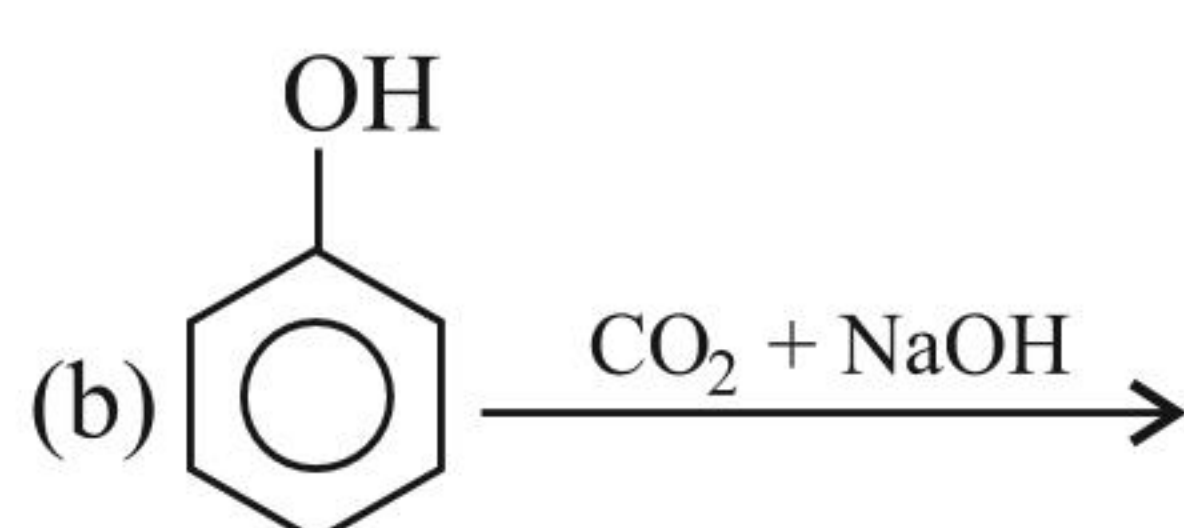
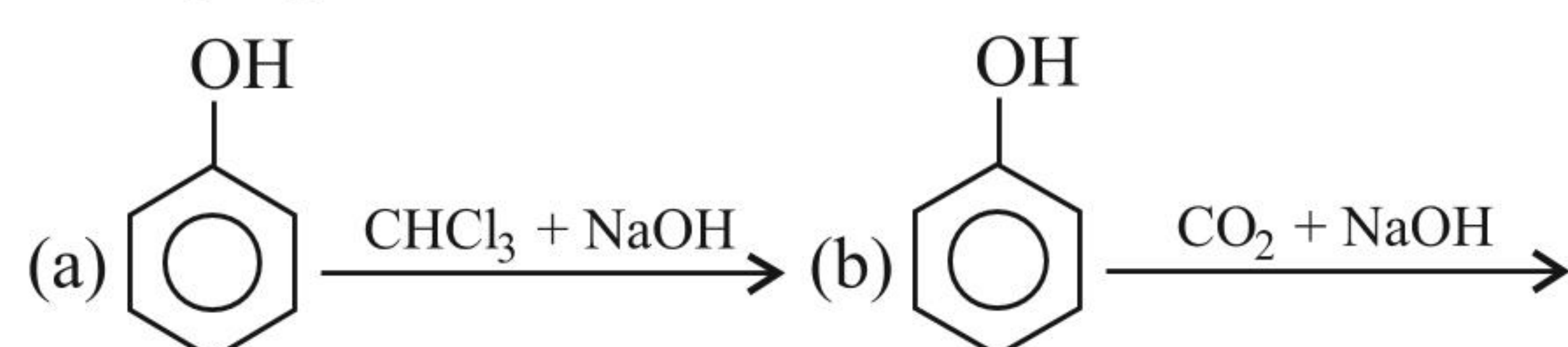
(1) 6

(2) 5

(3) 4

(4) 3

84. Identify number of reactions that would give salicylic acid as major product.



(2) 5

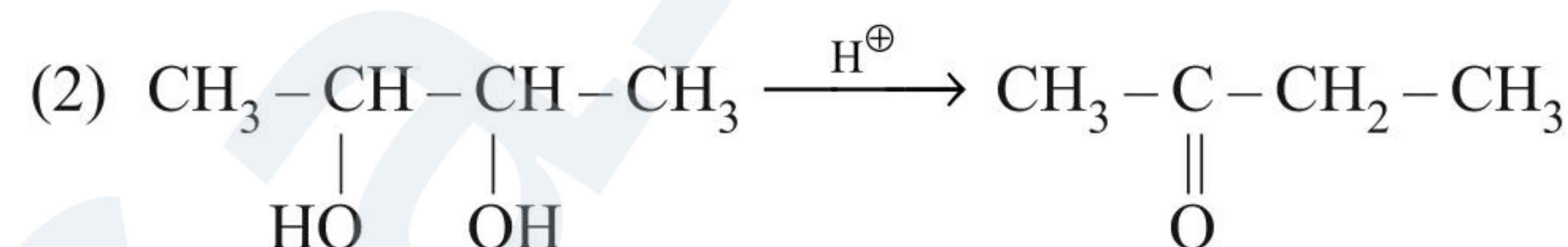
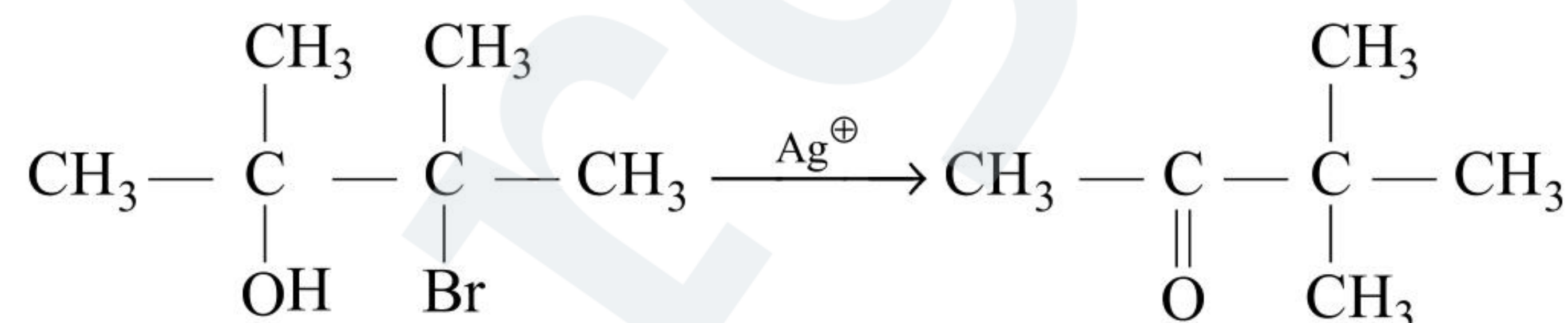
(1) 6

(3) 4

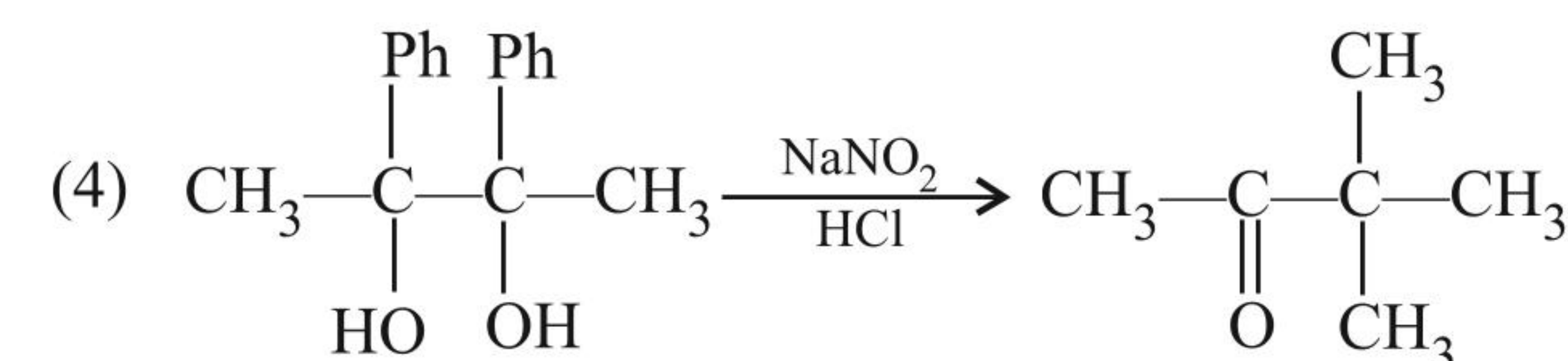
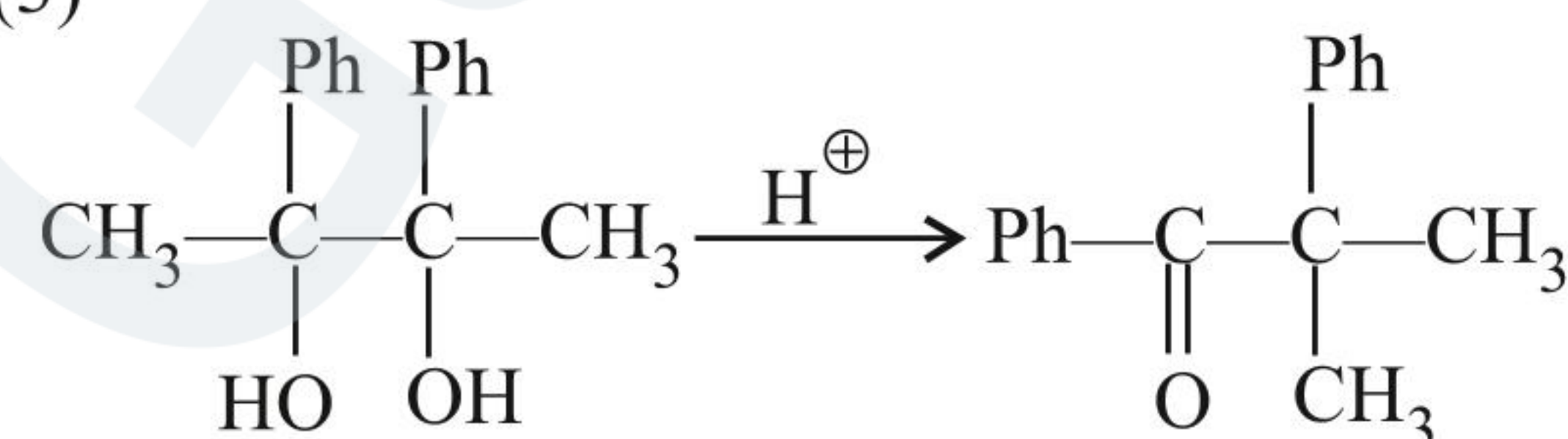
(4) 3

85. Which of the following does not represent the correct product?

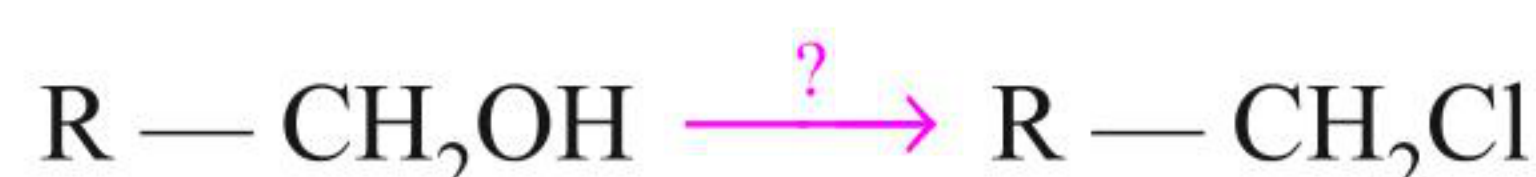
(1)



(3)



86. Find out the number of reagents that can be used for the following conversion,



- (a) HCl , ZnCl_2 , (b) PCl_3 , (c) PCl_5 , (d) POCl_3 , (e) SOCl_2 , (f) NaCl , (g) TsCl

(1) 4

(2) 5

(3) 6

(4) 7

Diols and Triols

87. Dioxane used as a solvent is obtained by distilling with

- (1) Glycerol, conc. H_2SO_4 (2) Glycerol, conc. H_3PO_4
(3) Glycol, conc. H_2SO_4 (4) Glycol, conc. H_3PO_4

88. Diethylene glycol is obtained by heating glycol with:

- (1) Conc. H_2SO_4 (2) Conc. H_3PO_4
(3) Aq. KOH (4) Conc. HNO_3

89. When glycerol is treated with a small amount of HI or PI_3 , the product obtained is:

- (1) Glycerol triiodide (2) Allyl iodide
(3) 2-Iodopropane (4) None

90. When glycerol is heated with a large amount of HI or PI_3 , the product obtained is:

- (1) Glycerol triiodide (2) Allyl iodide
(3) 2-Iodopropane (4) None

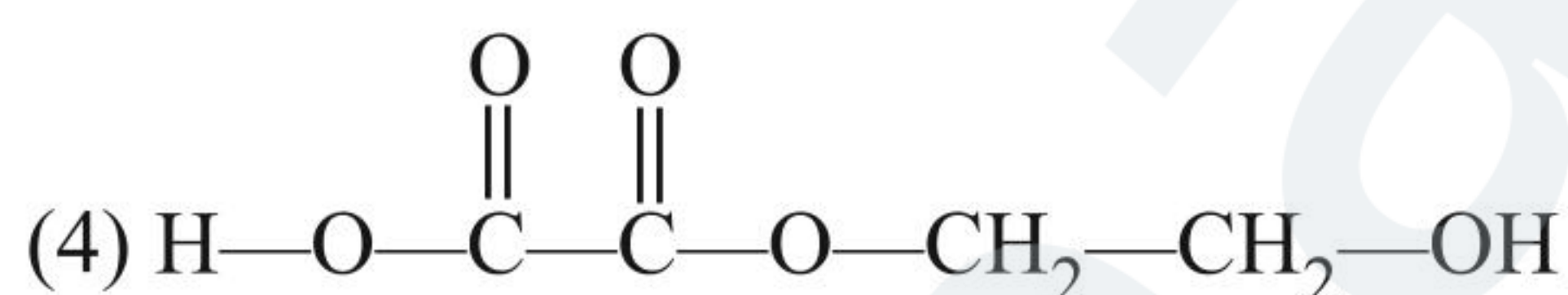
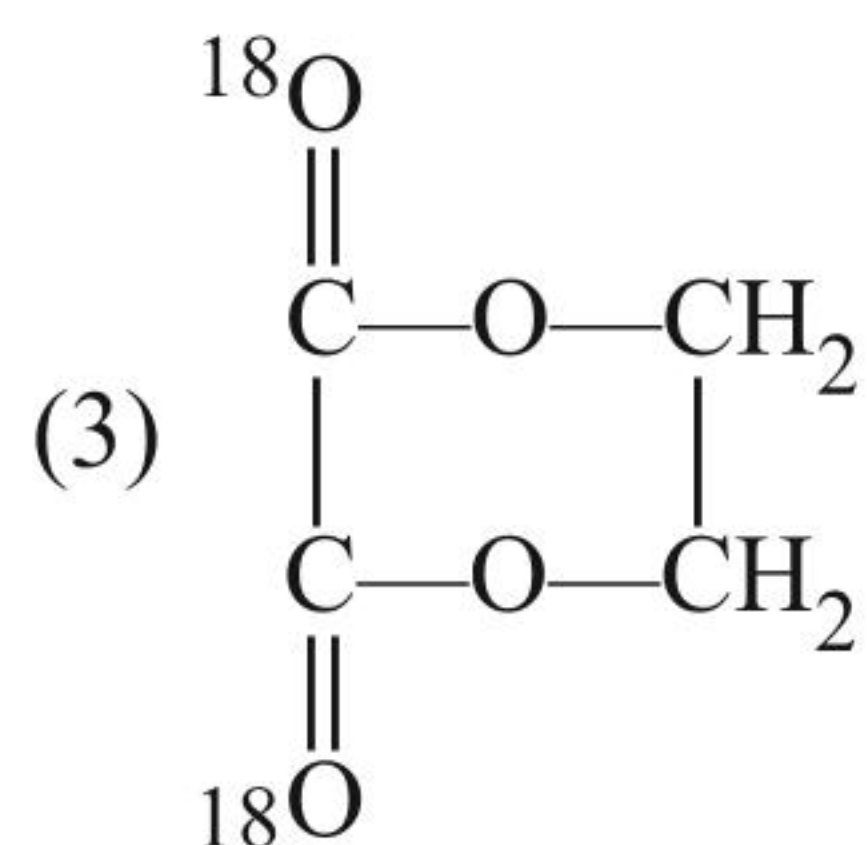
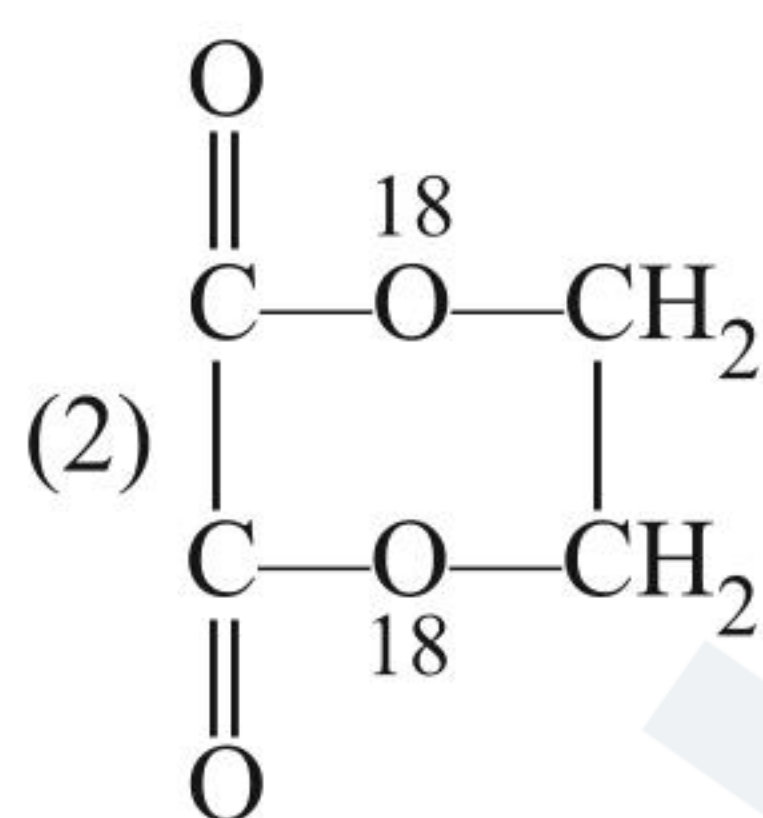
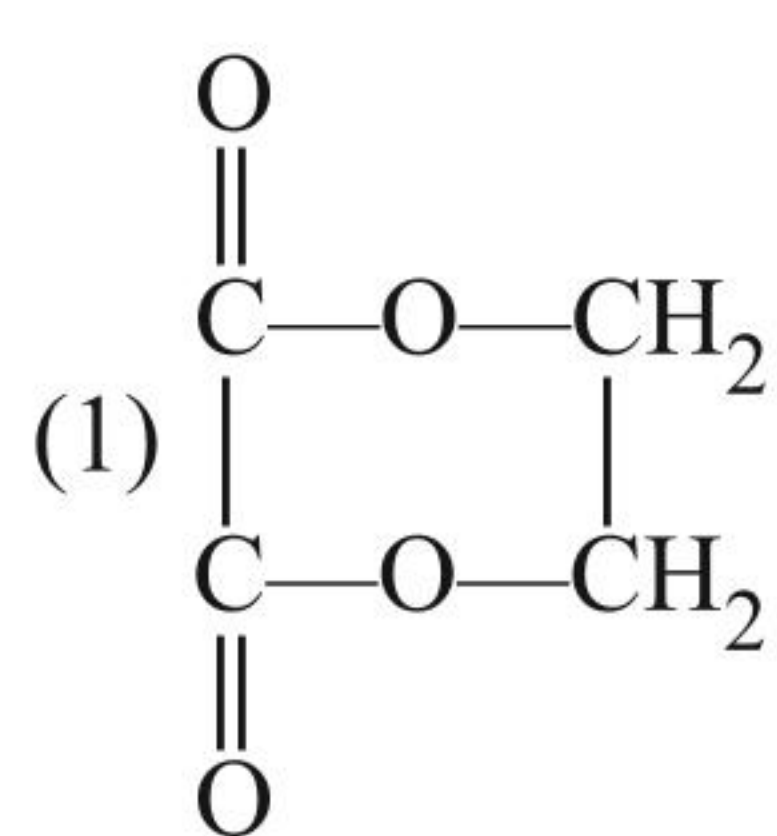
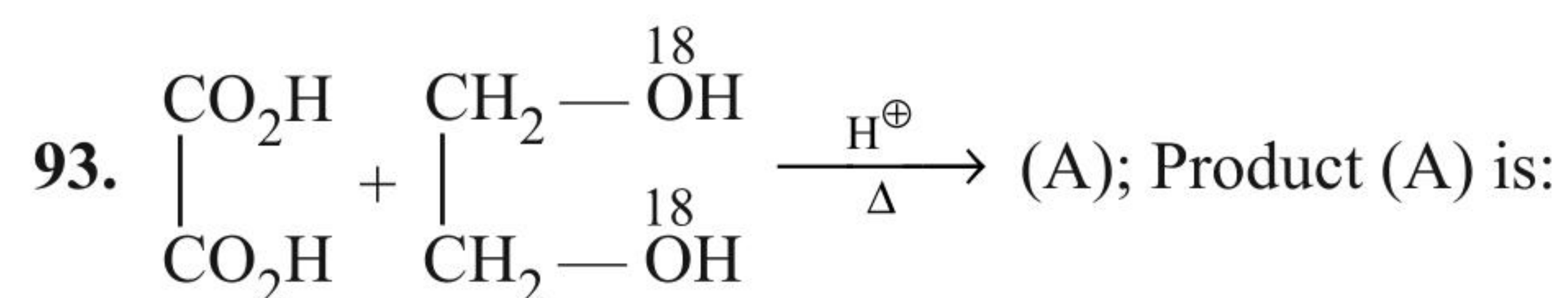
91. Dynamite is:

- (1) Mixture of glyceryl nitrate and dinitrate adsorbed on Keiselguhr.
- (2) Mixture of glyceryl dinitrate and trinitrate adsorbed on Keiselguhr.
- (3) Mixture of glyceryl nitrate and trinitrate adsorbed on Keiselguhr.
- (4) All

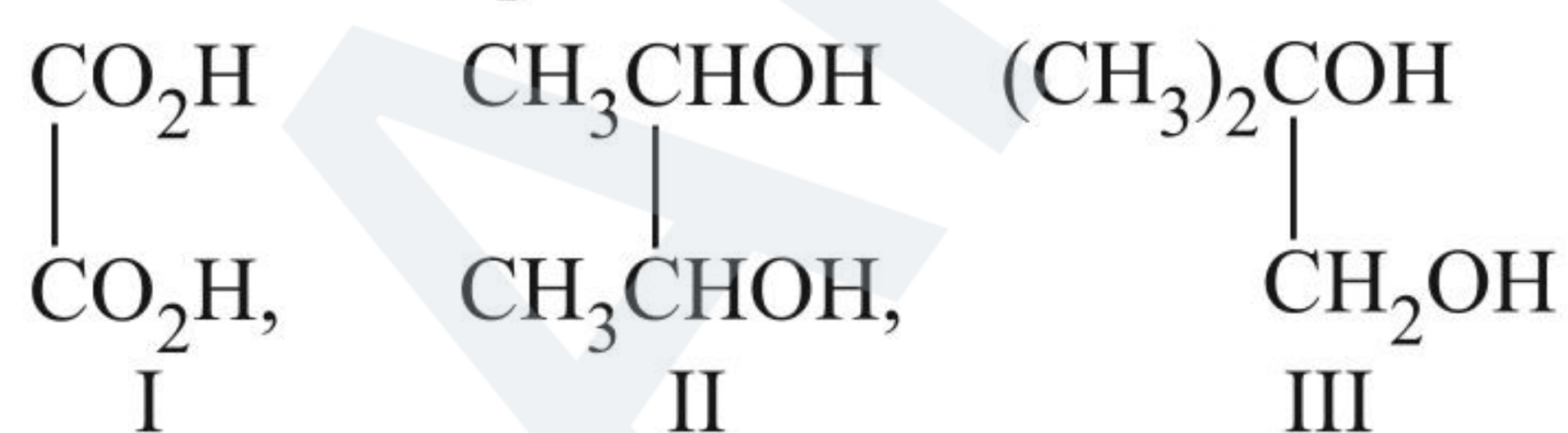
92. Which of the following statements is correct?

- i. Glycerol on reaction with oxalic acid at 110°C (383 K) and followed by heating and hydrolysis gives formic acid and glycerol.
- ii. Glycerol on reaction with oxalic acid at 230°C (503 K) and followed by heating gives allyl alcohol.
- iii. Glycerol on oxidation with dil. HNO_3 gives a mixture of glyceric and tartaric acid.
- iv. Glycerol on oxidation with conc. HNO_3 gives glyceric acid.

- (1) i and ii
- (2) i and iii
- (3) iii and iv
- (4) i, ii, iii, iv

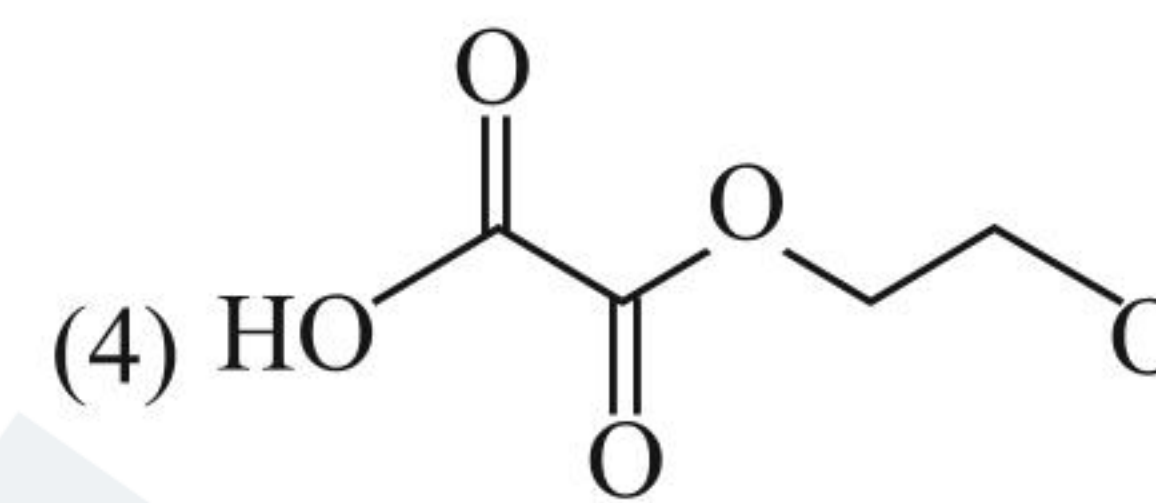
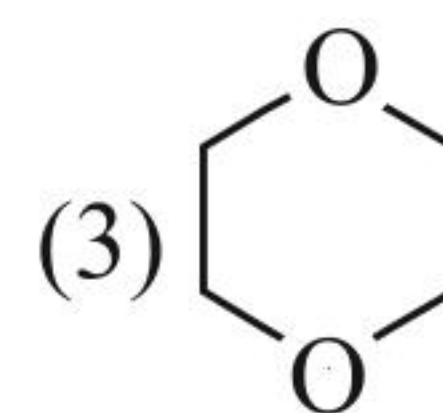
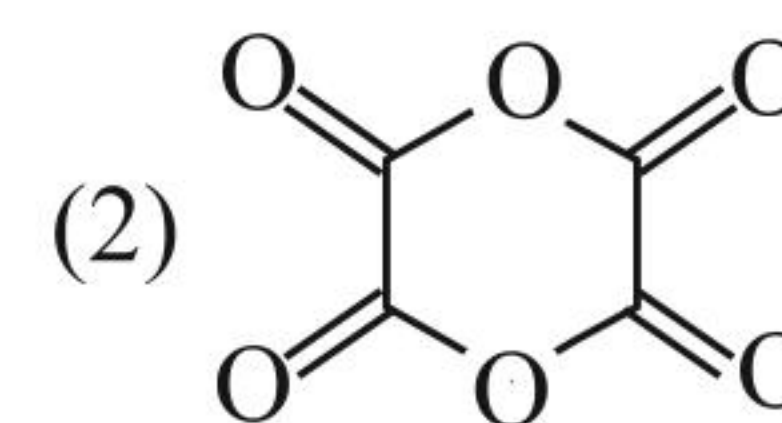
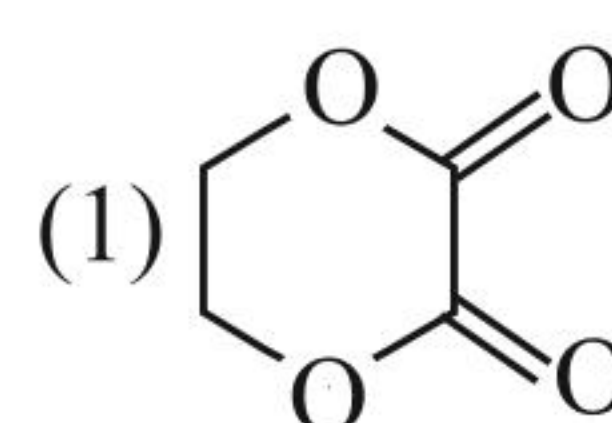


94. Arrange the following glycols in order of decreasing rate of oxidation with periodic acid.

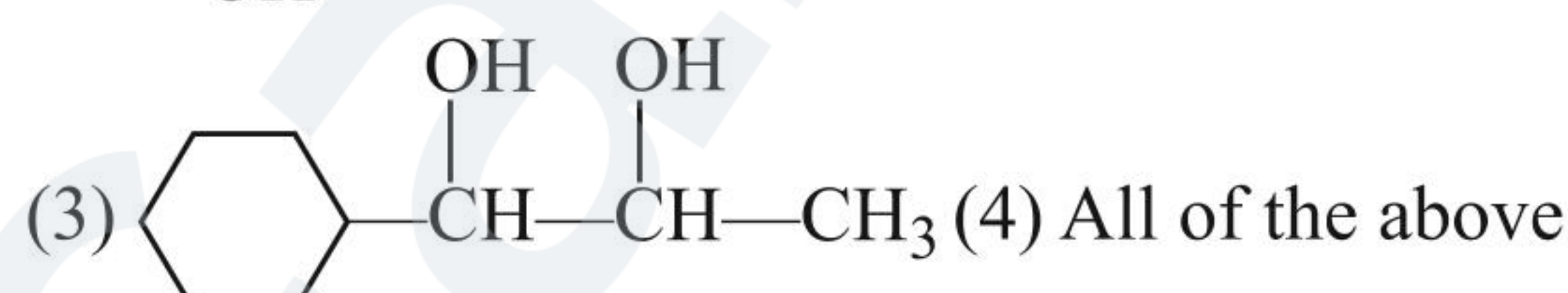
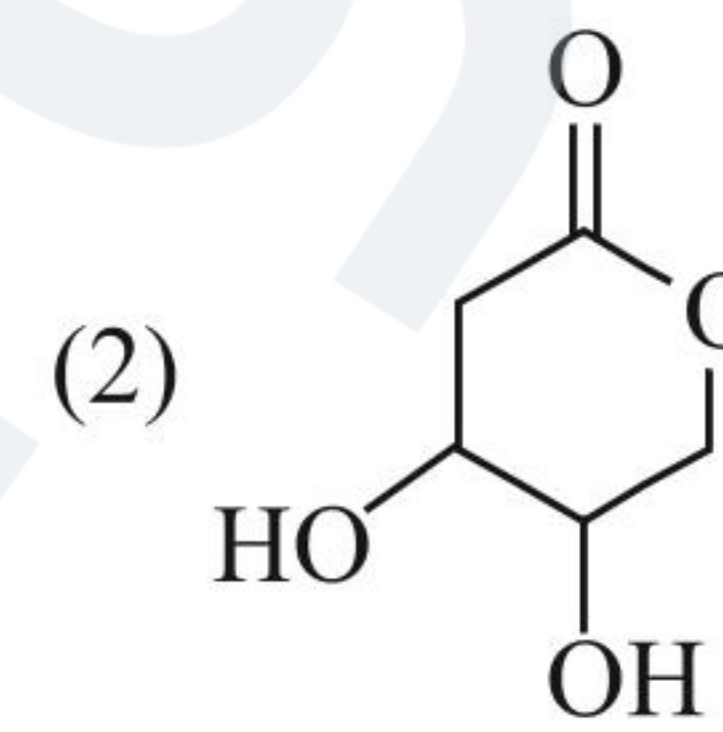
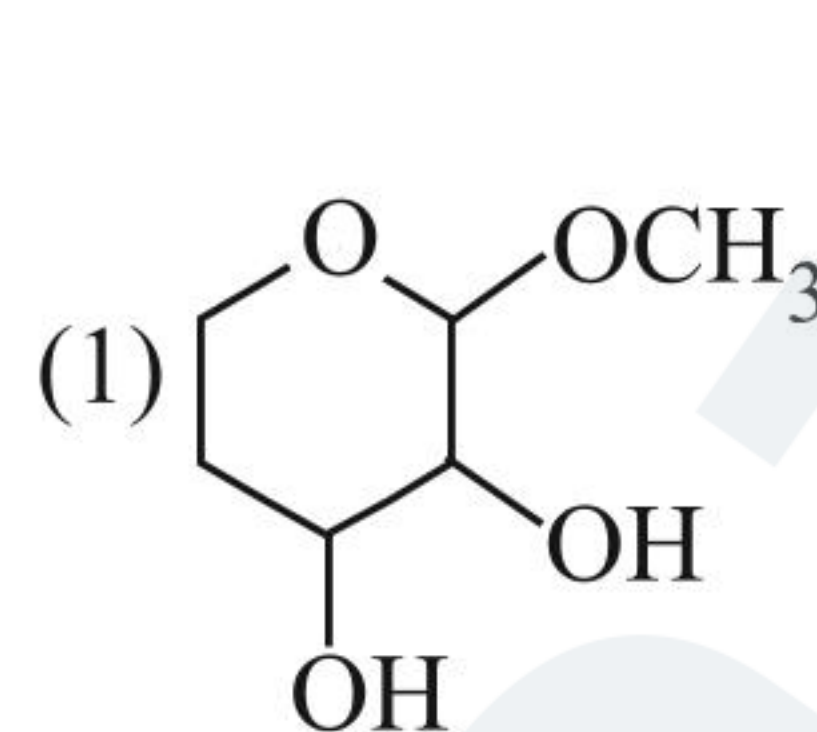


- (1) I > II > III
- (2) II > III > I
- (3) III > II > I
- (4) All will be oxidised at the same rate.

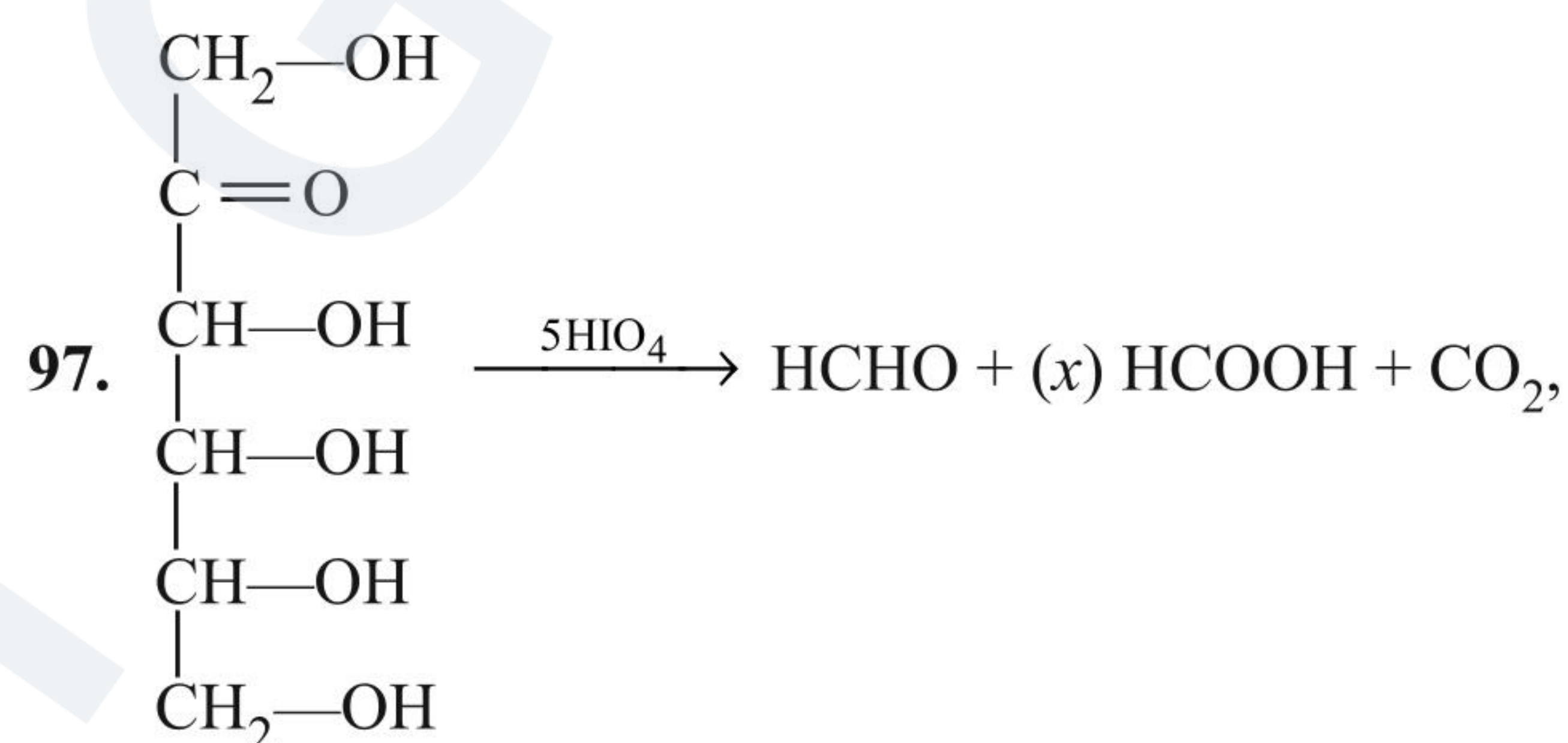
95. When ethylene glycol is heated with oxalic acid in the presence of conc. H_2SO_4 , the product formed is:



96. Which of the following compounds undergo periodic oxidation?



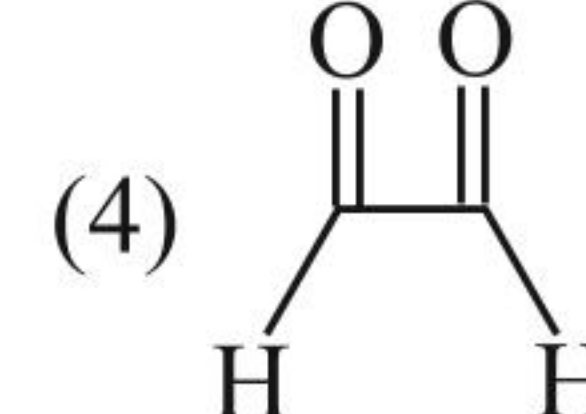
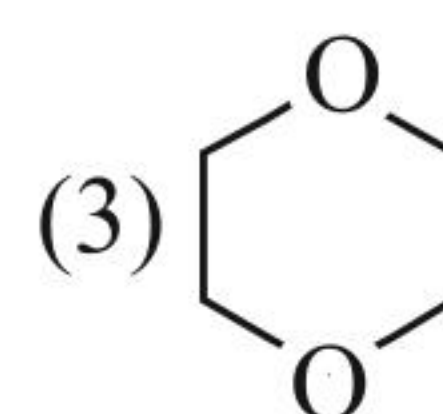
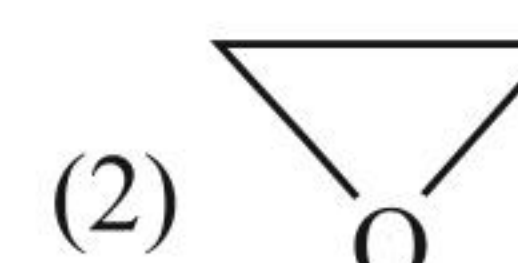
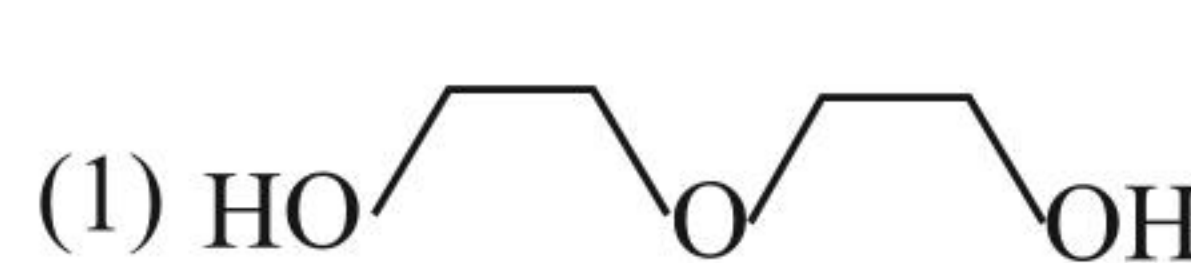
(4) All of the above



find out the value of (x).

- (1) 5
- (2) 4
- (3) 3
- (4) 2

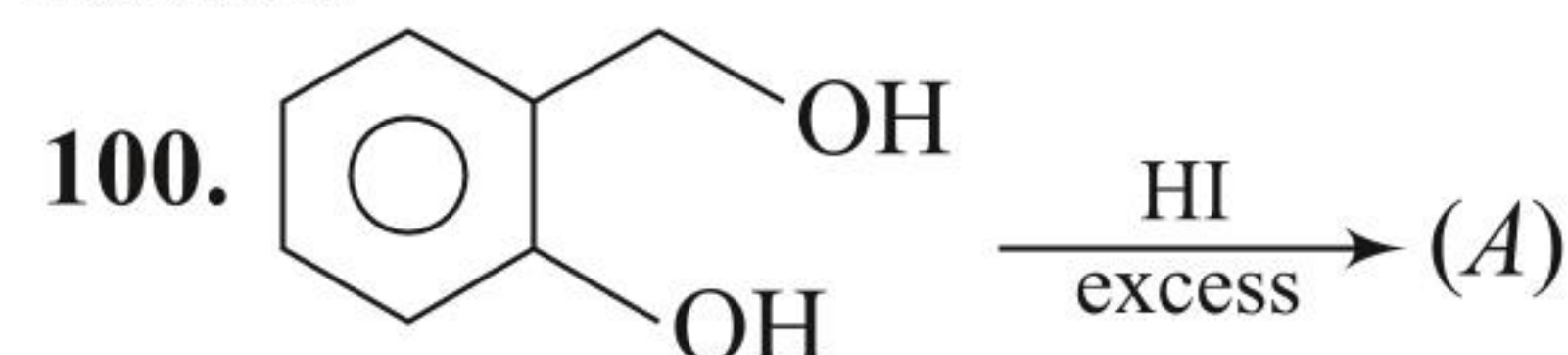
98. Ethylene glycol ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$) on heating with conc. H_2SO_4 gives mainly:



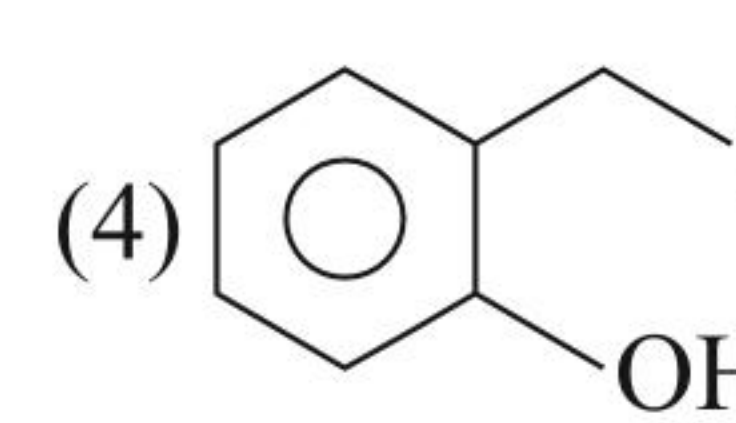
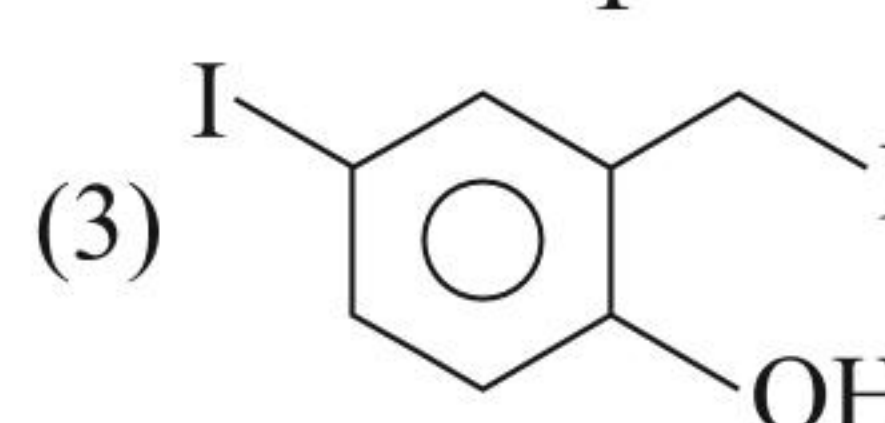
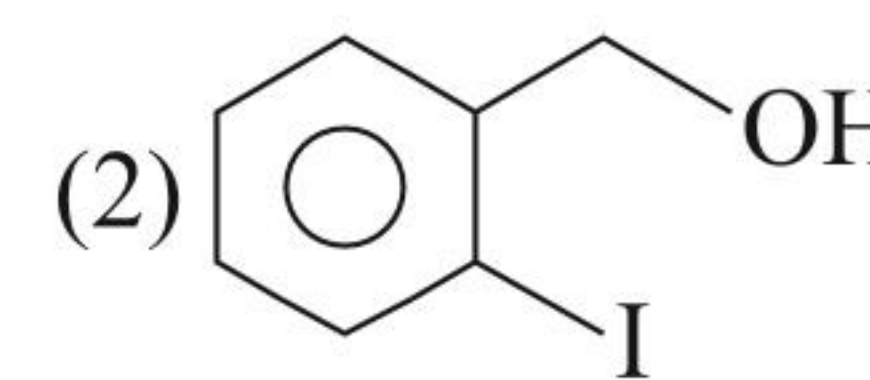
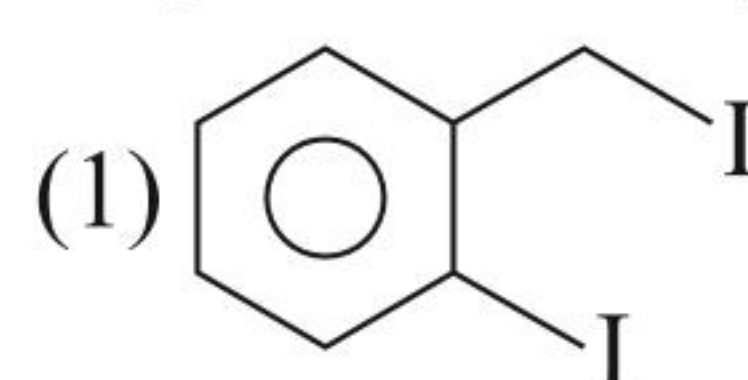
99. How many moles of HI reacts with glycerol to give 2-iodopropane?

- (1) 6
- (2) 5
- (3) 4
- (4) 3

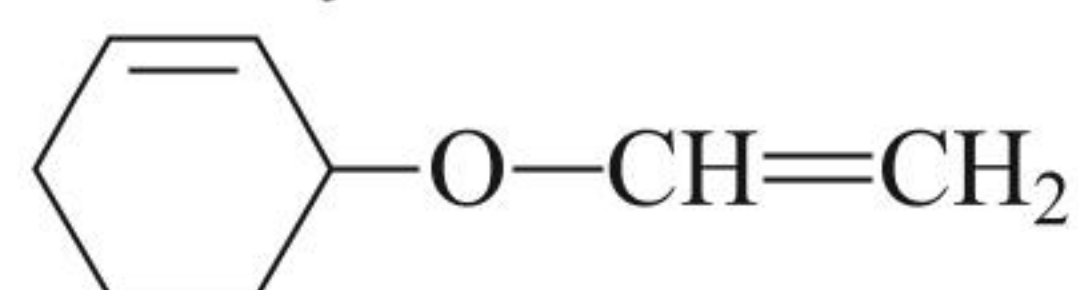
Ethers



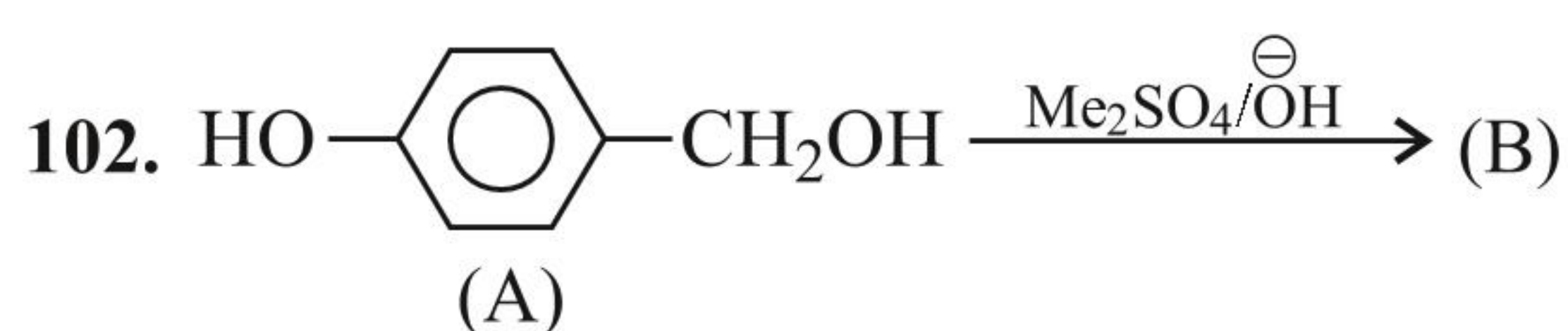
Major Product (A) is



101. The best method for synthesis of given ether by Williamson's ether synthesis is:

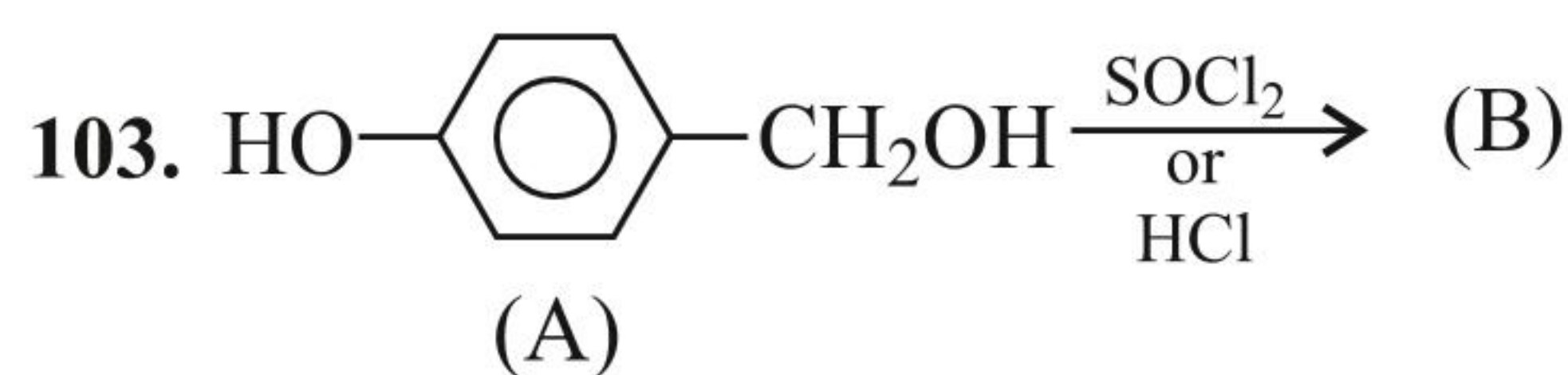


- (1) $\text{Cyclohexyl-O}^\ominus + \text{H}_2\text{C=CHCl}$
 (2) $\text{Cyclohexyl-O}^\oplus + \text{H}_2\text{C=CH-Cl}$
 (3) $\text{Cyclohexyl-Cl} + \text{H}_2\text{C=CH-O}^\ominus$
 (4) $\text{Cyclohexyl-Cl} + \text{H}_2\text{C=CH-O}^\oplus$



The product (B) is:

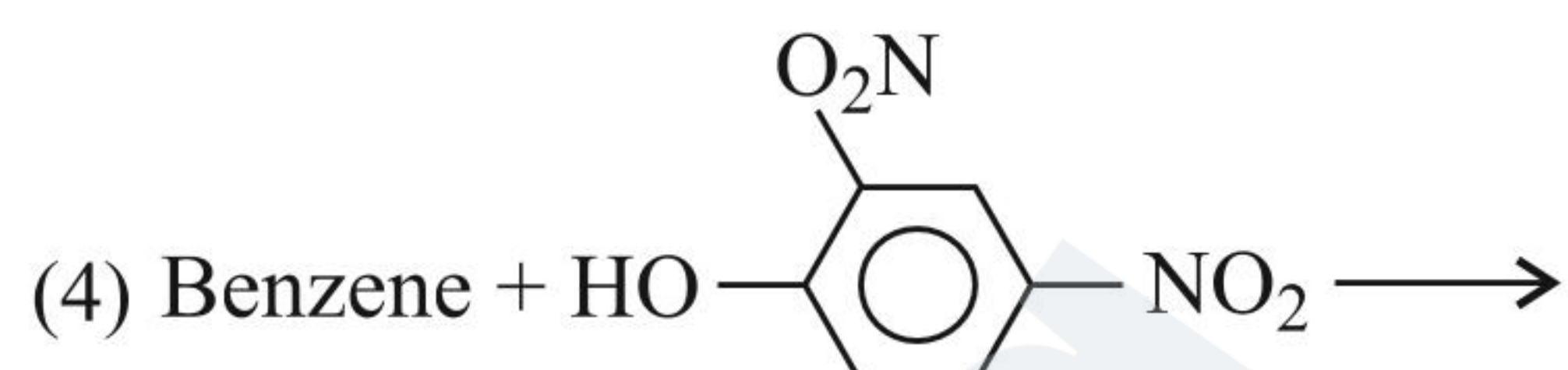
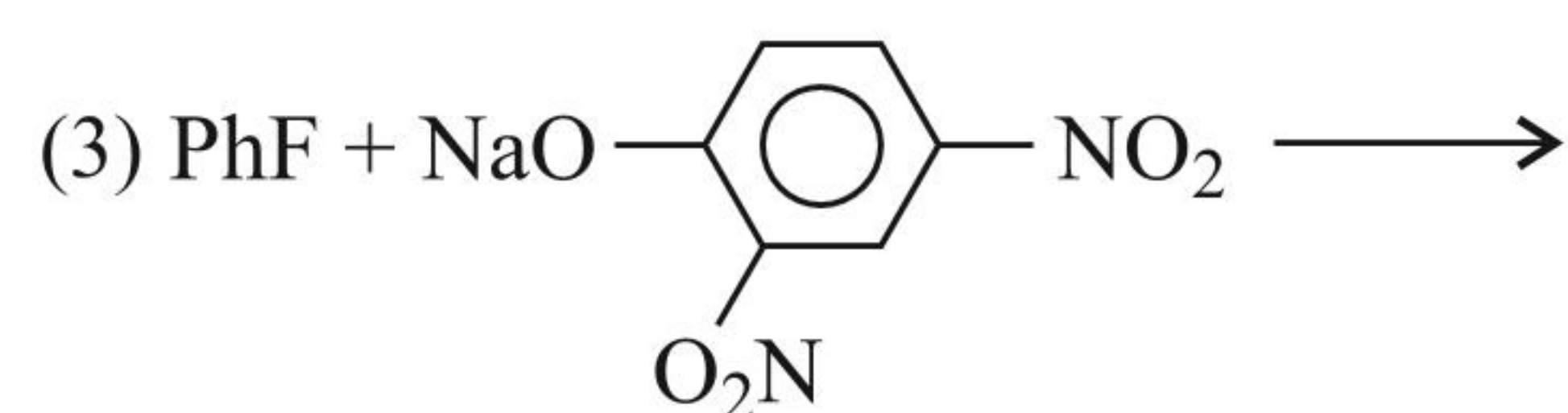
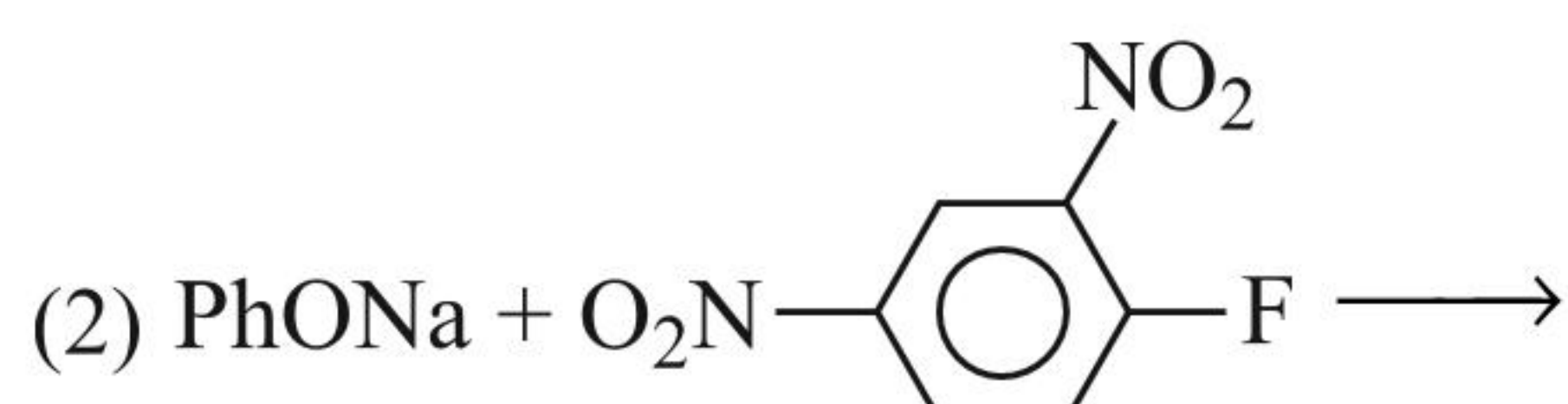
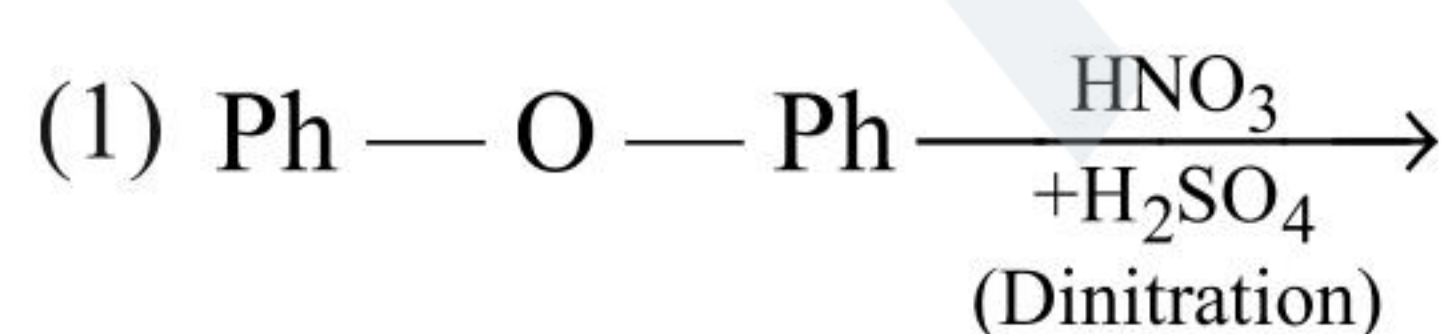
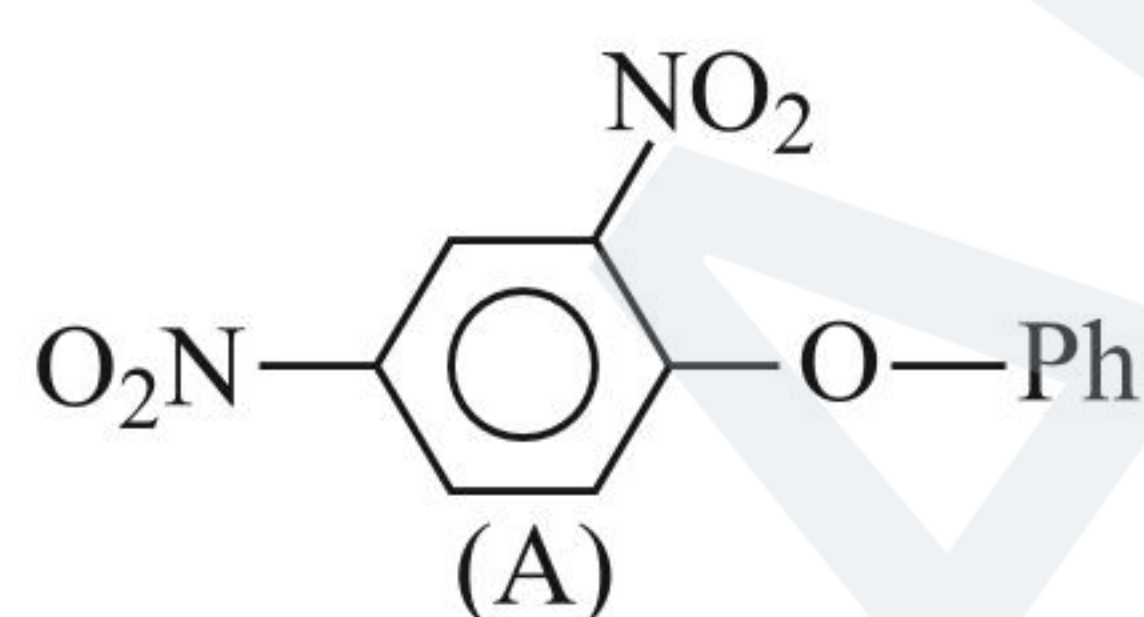
- (1) $\text{HO-C}_6\text{H}_4\text{-CH}_2\text{OMe}$
 (2) $\text{MeO-C}_6\text{H}_4\text{-CH}_2\text{OH}$
 (3) $\text{MeO-C}_6\text{H}_4\text{-CH}_2\text{OMe}$
 (4) All



The product (B) is:

- (1) $\text{HO-C}_6\text{H}_4\text{-CH}_2\text{Cl}$ (2) $\text{Cl-C}_6\text{H}_4\text{-CH}_2\text{OH}$
 (3) $\text{Cl-C}_6\text{H}_4\text{-CH}_2\text{Cl}$ (4) All

104. Which of the following is the best synthesis of the ether (A) shown below:



105. The crown ethers are heterocyclic polyethers, usually with at least four oxygen atoms. The 12-crown-4 ether contains carbon atoms.

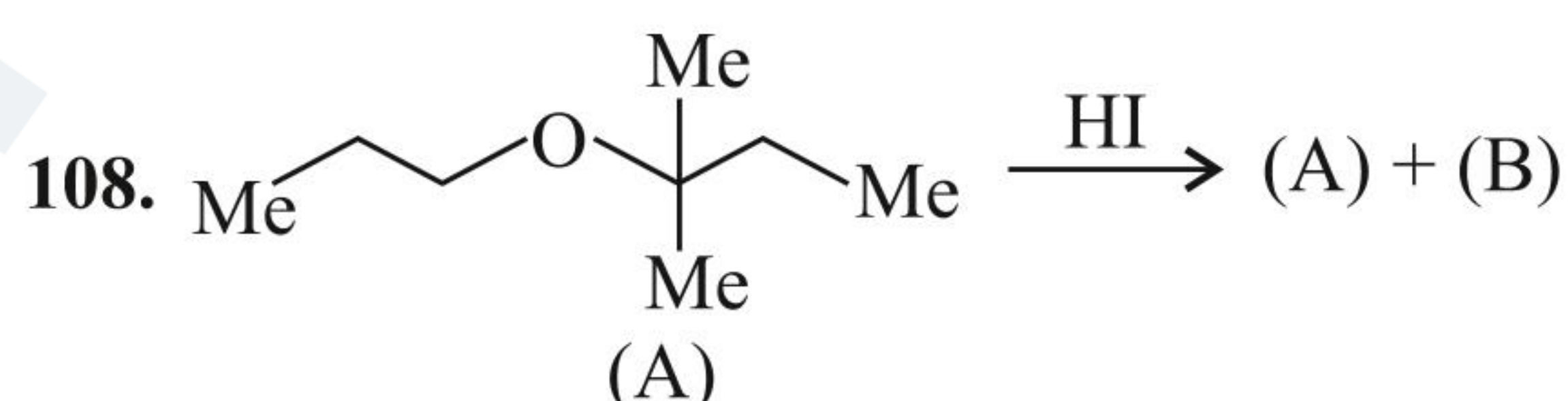
- (1) 12 (2) 4
 (3) 8 (4) 16

106. The crown-guest complex is called an inclusion compound. The crown ether allows the inorganic salt to dissolve in non-polar solvents. KMnO_4 forms a complex with crown ether. In this complex, the host is and the guest is

- (1) K^\oplus and crown ether (2) Crown ether and K^\oplus
 (3) MnO_4^\ominus and crown ether (4) Crown ether and MnO_4^\ominus

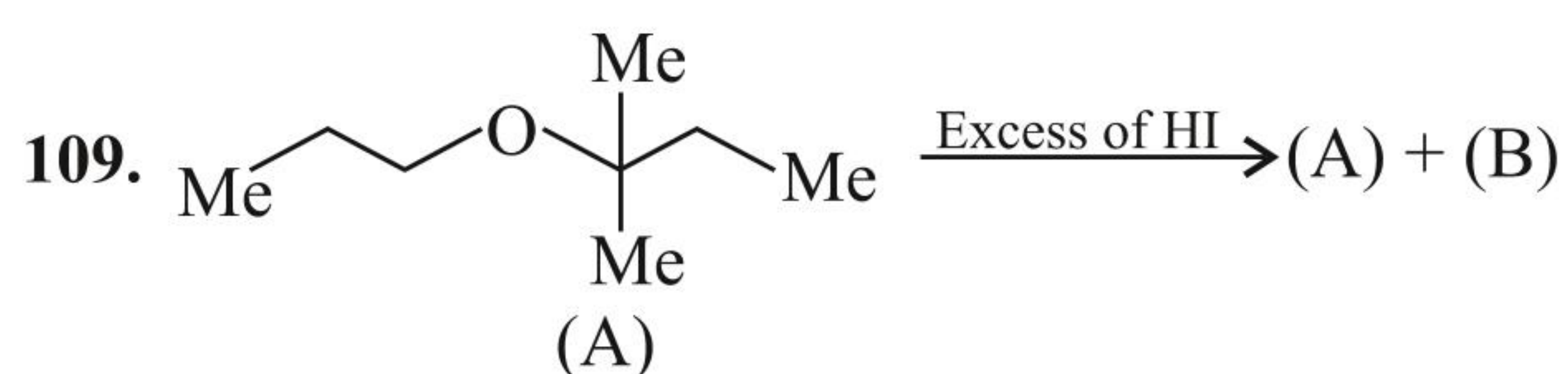
107. The presence of peroxides in old samples of ethers is detected by shaking them with a freshly prepared solution of Fe^{2+} (FeSO_4) followed by the addition of KCNS. The appearance of colour indicates the presence of peroxides.

- (1) Blue (2) Green
 (3) Red (4) Brown



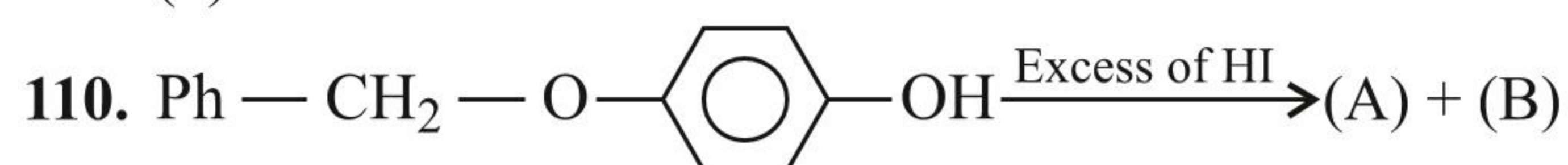
The products (A) and (B) are:

- A** **B**
 (1) $\text{Me-CH}_2\text{-CH}_2\text{-OH}$ and $\text{I-C(Me)}_2\text{-CH}_2\text{-Me}$
 (2) $\text{Me-CH}_2\text{-CH}_2\text{-I}$ and $\text{HO-C(Me)}_2\text{-CH}_2\text{-Me}$
 (3) $\text{Me-CH}_2\text{-CH}_2\text{-I}$ and $\text{I-C(Me)}_2\text{-CH}_2\text{-Me}$
 (4) All



The products (A) and (B) are:

- A** **B**
- (1) $\text{Me}-\text{CH}_2-\text{CH}_2-\text{OH}$ and $\text{I}-\text{C}(\text{Me})_2-\text{CH}_2-\text{Me}$
- (2) $\text{Me}-\text{CH}_2-\text{CH}_2-\text{I}$ and $\text{HO}-\text{C}(\text{Me})_2-\text{CH}_2-\text{Me}$
- (3) $\text{Me}-\text{CH}_2-\text{CH}_2-\text{I}$ and $\text{I}-\text{C}(\text{Me})_2-\text{CH}_2-\text{Me}$
- (4) All



The products (A) and (B) are:

- A** **B**
- (1) $\text{PhCH}_2\text{OH} + \text{I}-\text{C}_6\text{H}_4-\text{OH}$
- (2) $\text{PhCH}_2\text{I} + \text{HO}-\text{C}_6\text{H}_4-\text{OH}$
- (3) $\text{PhCH}_2\text{I} + \text{I}-\text{C}_6\text{H}_4-\text{OH}$
- (4) $\text{PhCH}_2\text{OH} + \text{I}-\text{C}_6\text{H}_4-\text{I}$



The product (A) is:

- (1) $\text{CH}_3-\underset{\text{OOH}}{\text{CH}}-\text{O}-\text{CH}_2-\text{CH}_3$
- (2) $\underset{\text{OOH}}{\text{CH}_2}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$
- (3) $\text{CH}_3-\underset{\text{OOH}}{\text{CH}}-\text{O}-\underset{\text{OOH}}{\text{CH}}-\text{CH}_3$
- (4) $\underset{\text{OOH}}{\text{CH}_2}-\text{CH}_2-\text{O}-\text{CH}_2-\underset{\text{OOH}}{\text{CH}_2}$

112. Which of the following statements is/are **wrong**?

- (1) When diethyl ether is treated with excess of Cl_2 in light, perchloro diethyl ether is obtained $(\text{C}_2\text{Cl}_5)_2\text{O}$.
- (2) When diethyl ether is treated with 1 mol of Cl_2 in dark, 1-chloro ethyl ether is obtained.
- (3) When diethyl ether is treated with 2 mol of Cl_2 in dark, 1,1'-dichlorodiethyl is obtained.
- (4) When diethyl ether is treated with 2 mol of Cl_2 in dark, 1,1'-dichloro and 1,2-dichloroethyl ether are obtained.

113. Which of the following reactions is possible?

- (1) $\text{Me}_3\text{C}-\text{ONa} + \text{Me}_3\text{C}-\text{Br} \rightarrow \text{Me}_3\text{C}-\text{O}-\text{CMe}_3$

- (2) $\text{Me}_2\text{CH}-\text{ONa} + \text{Me}_2\text{CHBr} \rightarrow \text{Me}_2\text{CH}-\text{O}-\text{CHMe}_2$
- (3) $\text{PhONa} + \text{PhBr} \rightarrow \text{PhOPh}$
- (4) $\text{PhONa} + \text{CH}_3\text{Br} \rightarrow \text{PhOCH}_3$

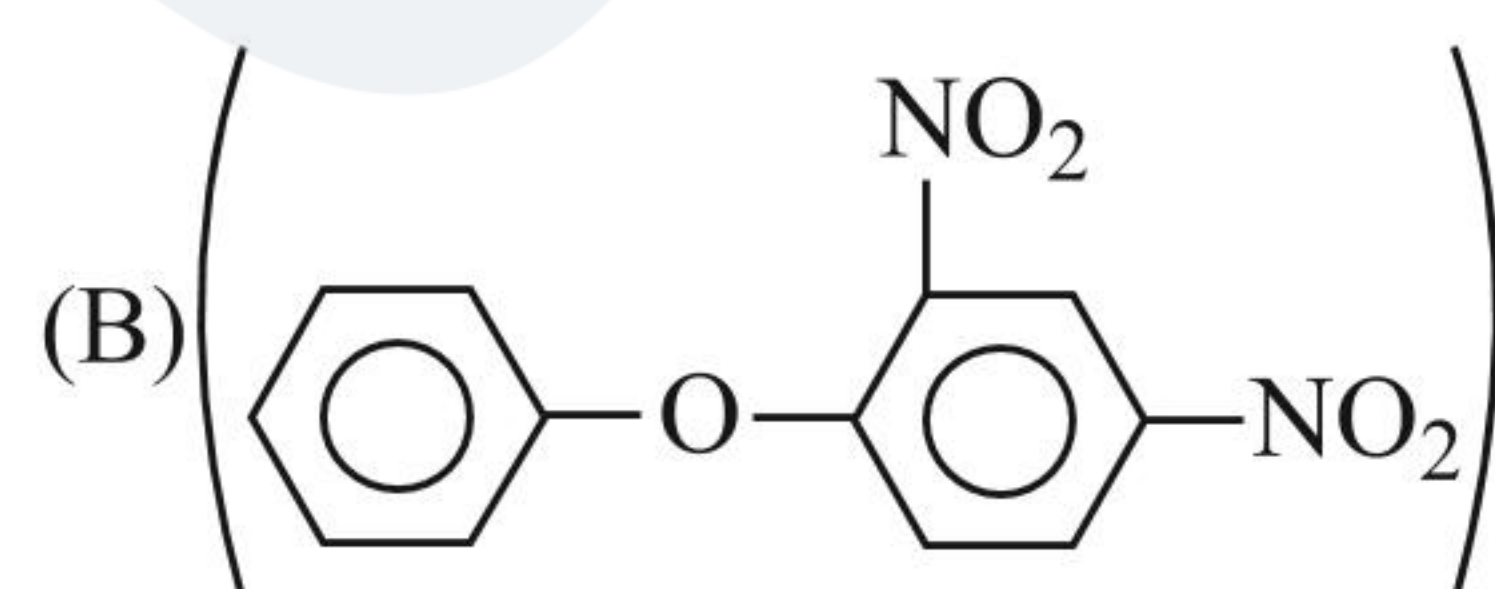
114. Which of the following reactions is possible?

- (1) $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{ONa} + (\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br} \rightarrow (\text{CH}_3)_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}(\text{CH}_3)_3$
- (2) $\text{CH}_3\text{CH}=\text{CH}-\text{ONa} + \text{CH}_3\text{CH}=\text{CH}-\text{Br} \rightarrow \text{CH}_3\text{CH}=\text{CH}-\text{O}-\text{CH}=\text{CH}-\text{CH}_3$
- (3) $(\text{CH}_3)_3\text{C}-\text{ONa} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_3$
- (4) $\text{CH}_3\text{CH}_2\text{ONa} + \text{PhBr} \rightarrow \text{CH}_3\text{CH}_2\text{O}-\text{Ph}$

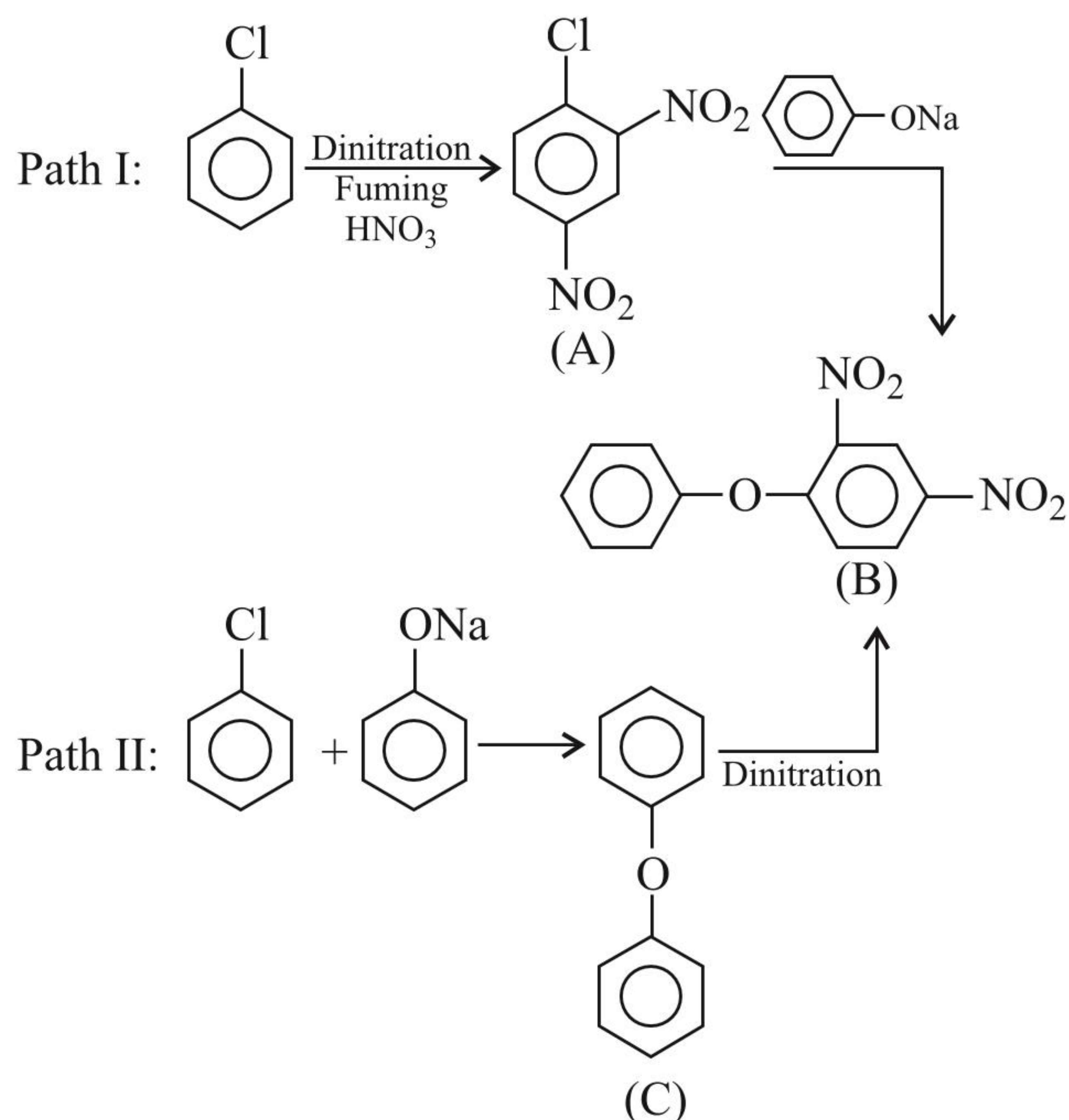
115. Give the decreasing order of reactivity of the following alkyl halides in the Williamson's reaction.

- i. $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$ ii. $\text{ClCH}_2\text{CH}=\text{CH}_2$
- iii. $\text{ClCH}_2\text{CH}_2\text{CH}_3$ iv. $\text{BrCH}_2\text{CH}_2\text{CH}_3$
- (1) ii > iv > iii > i (2) i > iii > iv > ii
- (3) ii > iii > iv > i (4) i > iv > iii > ii

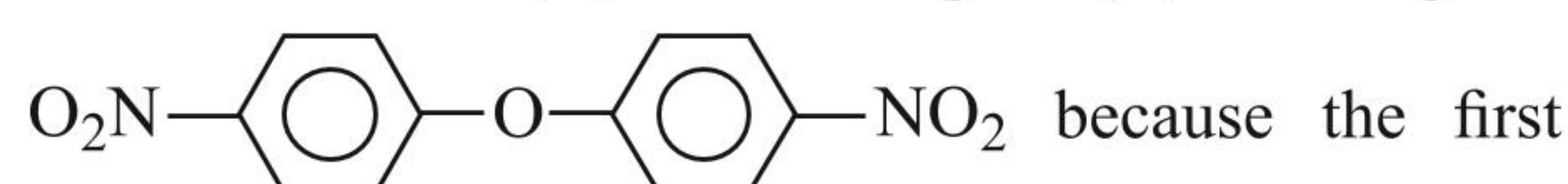
116. There are two paths (I and II) for the preparation of phenyl-2,4-dinitro phenyl ether.



Which of the following statements is true?

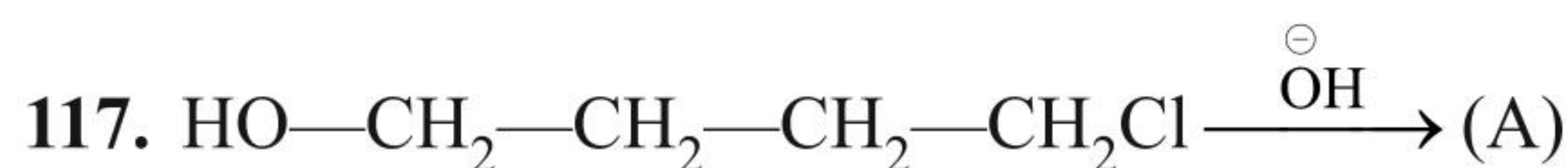


- i. Path I is feasible, whereas path II is not.
- ii. Path II is feasible, whereas path I is not.
- iii. The Cl of (A) undergoes S_N reaction because it is activated by the two EWG ($-\text{NO}_2$) groups.
- iv. The nitration of (C) does not give (B) but it gives



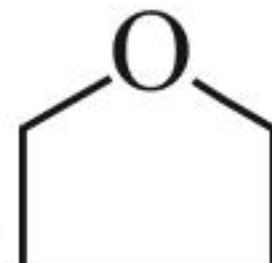
nitro group is deactivating, so the second nitro group enters the other ring.

- (1) i (2) ii
(3) i, iii, iv (4) i and iv



Which of the following statements is true?

i. The product (A) is $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$.

ii. The product (A) is  (tetrahydrofuran, THF)

iii. (A) is prepared by $\text{S}_{\text{N}}2$ reaction.

iv. (A) is prepared by intramolecular $\text{S}_{\text{N}}2$ reaction.

- (1) i (2) ii and iv
(3) i and iv (4) ii and iii



Which of the following statements is true about the above reaction?

i. The product is $\text{CH}_3\text{CH}_2\text{OCH}_3$.

ii. The strong acid HBF_4 first protonates CH_2N_2 to give CH_2N_2^+ , from which N_2 (an extremely good leaving group) is displaced.

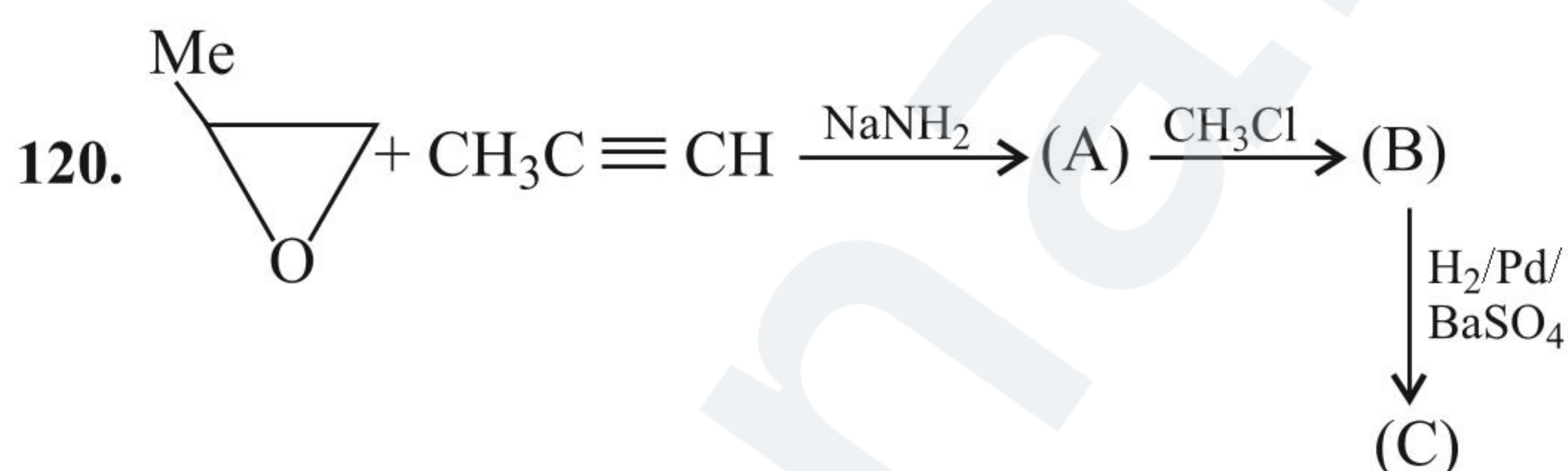
iii. $\text{CH}_3\text{CH}_2\text{OH}$ acts as a nucleophile.

iv. CH_2N_2 acts as a nucleophile.

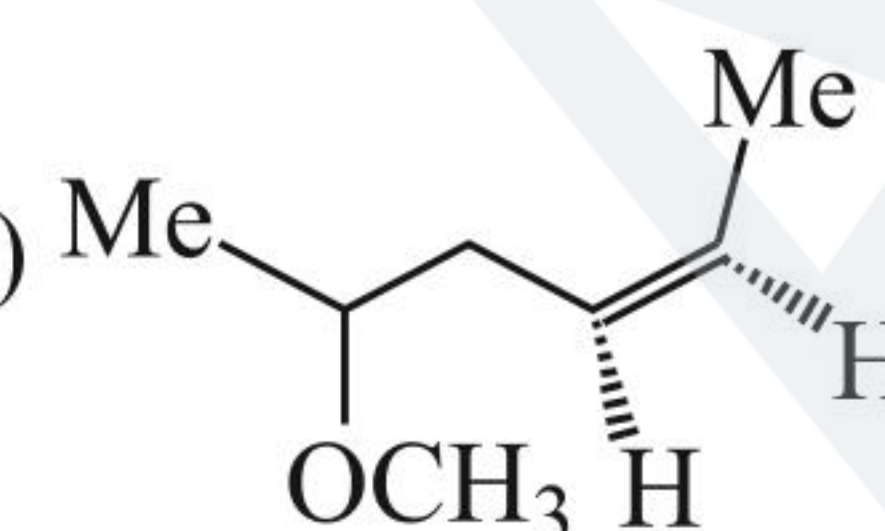
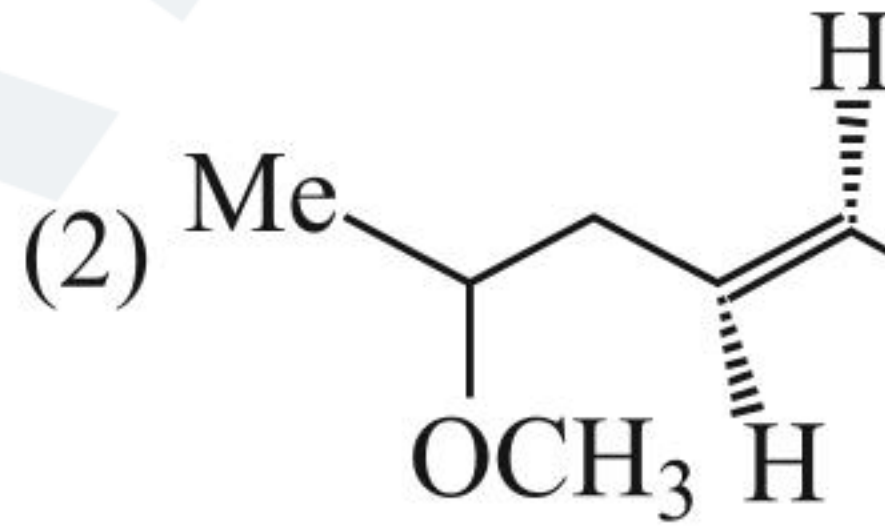
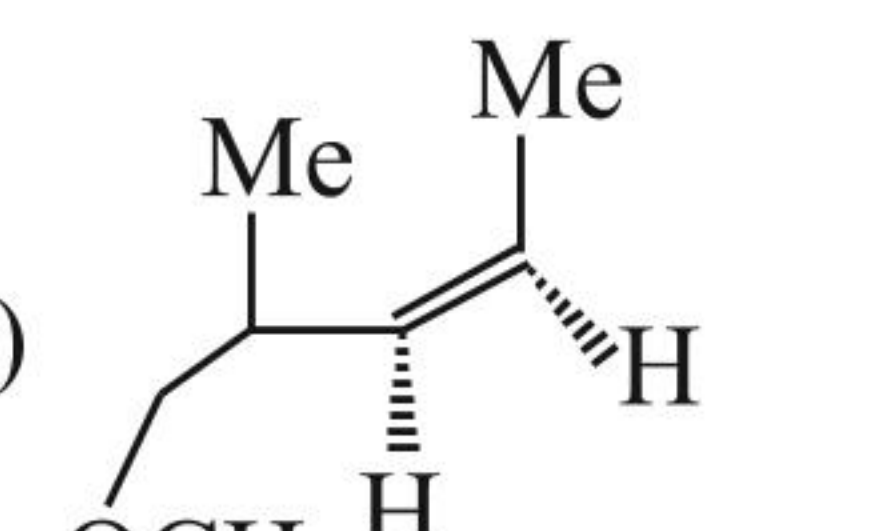
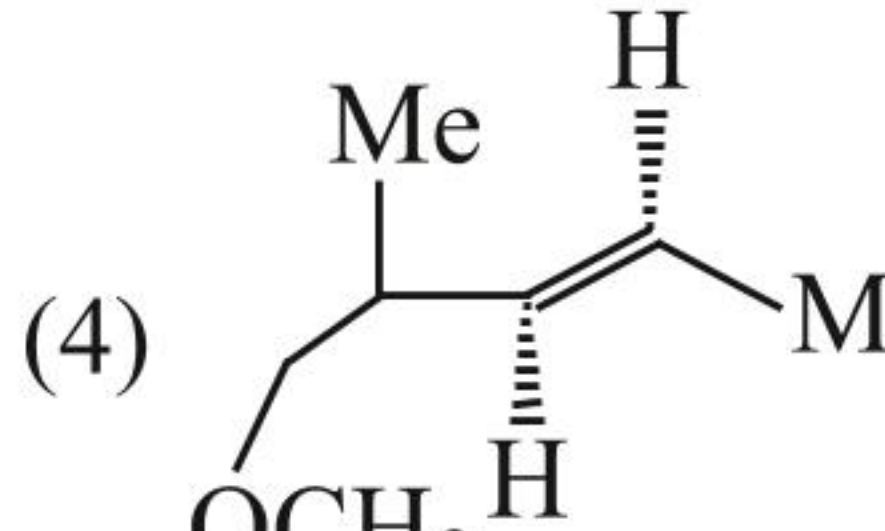
- (1) i and ii (2) i, ii, and iii
(3) i, ii, and iv (4) All



- (1) The product is $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$.
(2) The product is $\text{CH}_3-\text{O}-\text{CH}_3$.
(3) The product is $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$.
(4) All



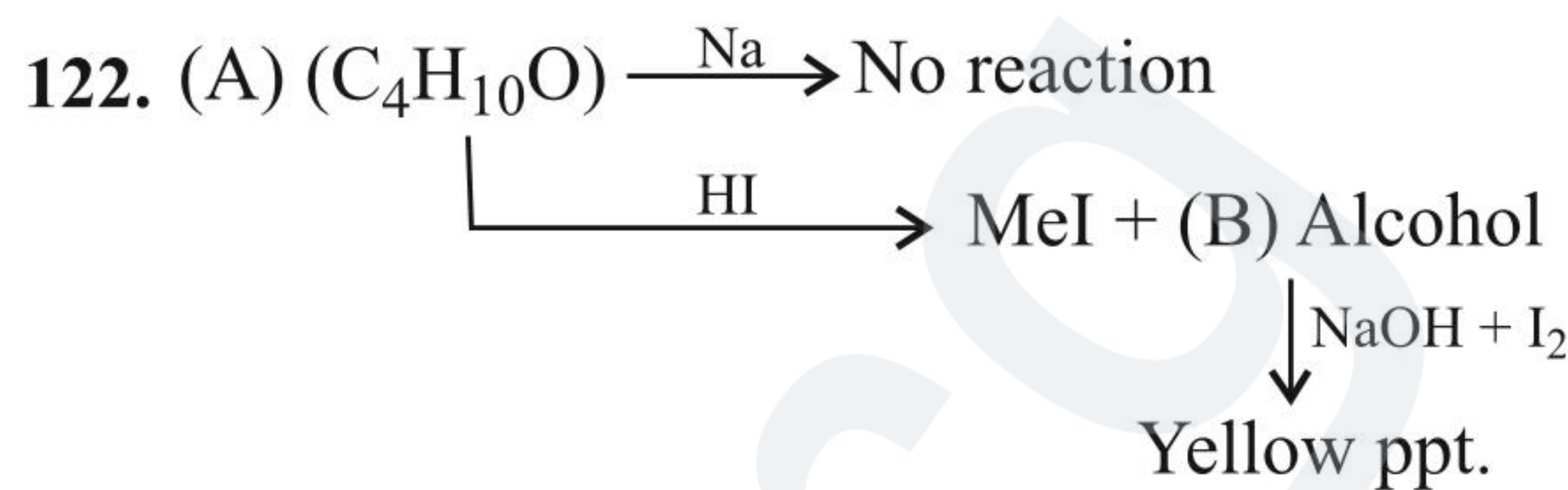
The product (C) is:

- (1)  (2) 
(3)  (4) 

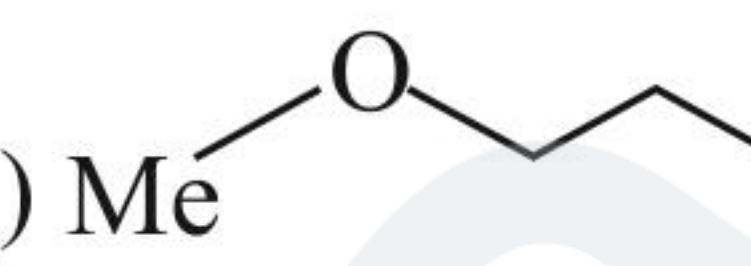
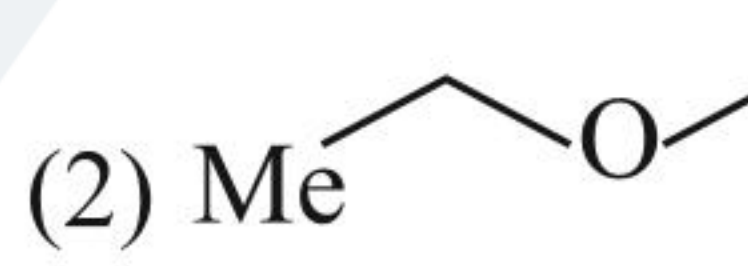
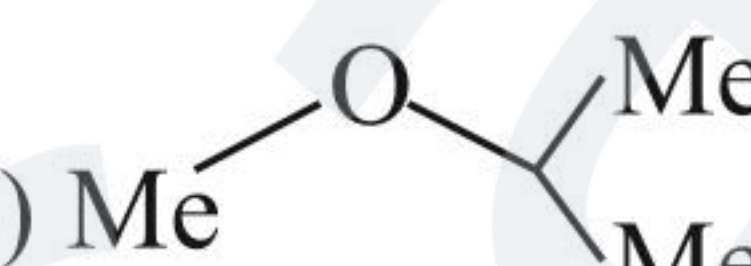
121. An organic compound (A) with molecular formula $\text{C}_7\text{H}_8\text{O}$ dissolves in NaOH and gives characteristic colour with

FeCl_3 . On treatment with Br_2 , it gives a tribromo product $\text{C}_7\text{H}_5\text{OBr}_3$. The compound is:

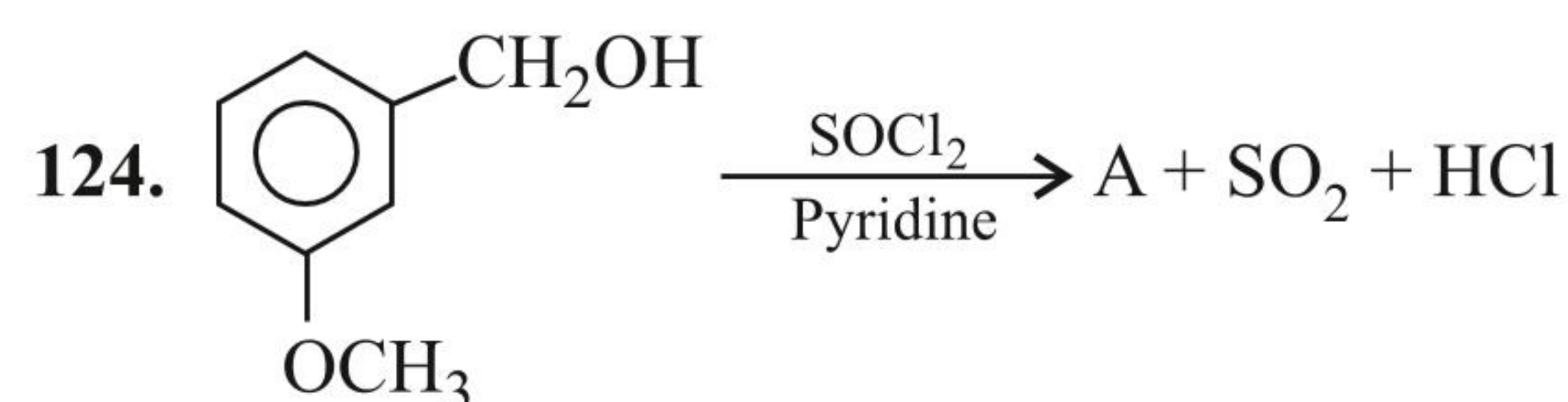
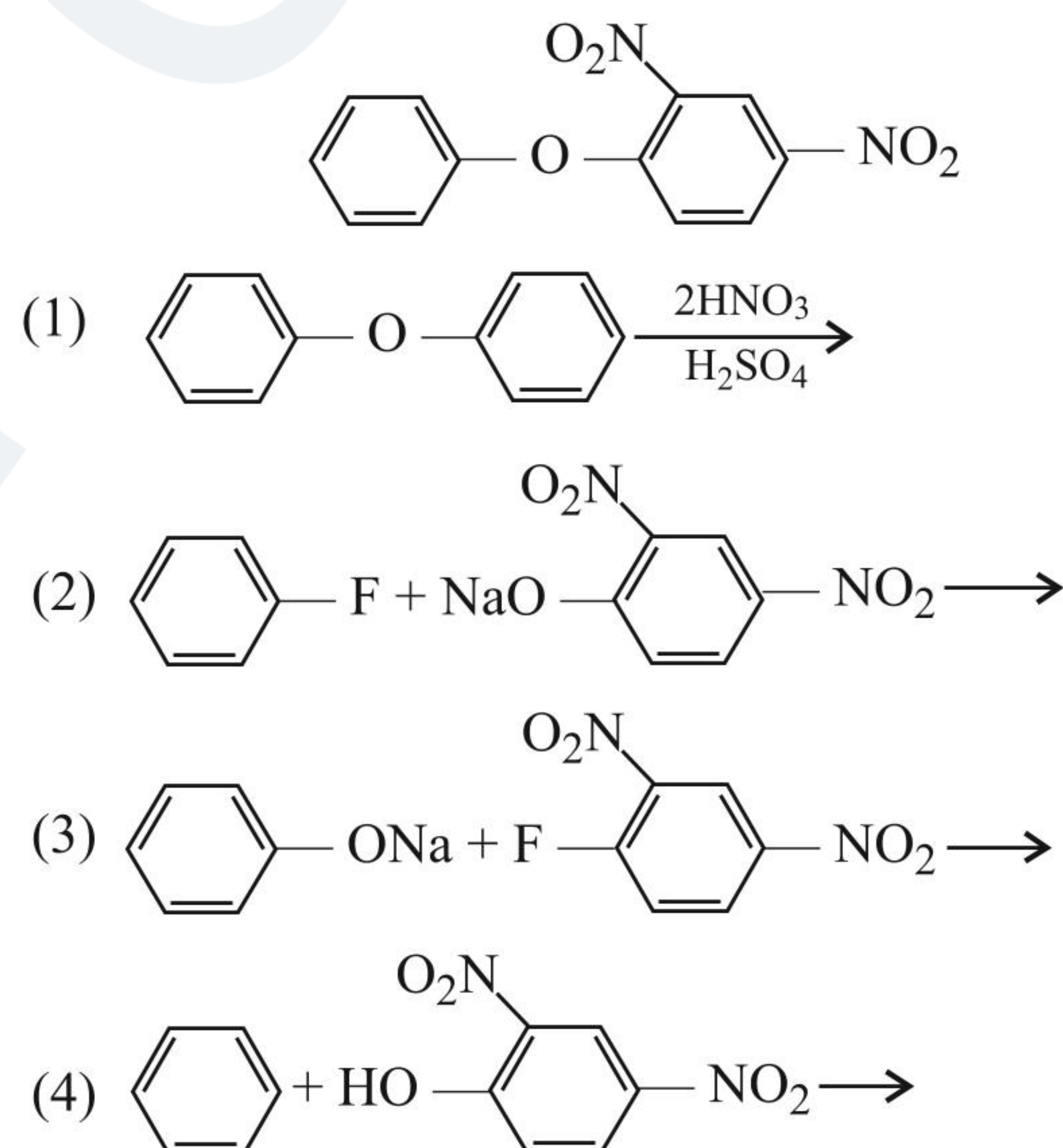
- (1) *p*-Hydroxybenzene
(2) 2-Methoxy-2-phenyl propane
(3) *m*-Cresol
(4) *p*-Cresol



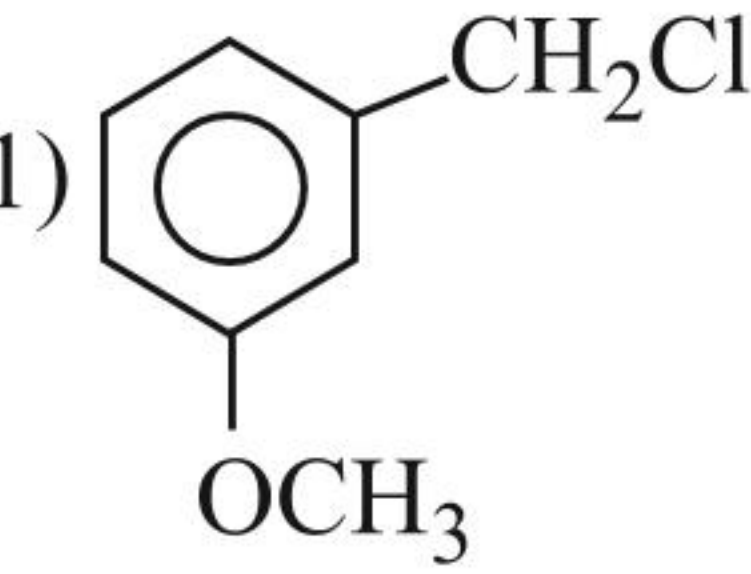
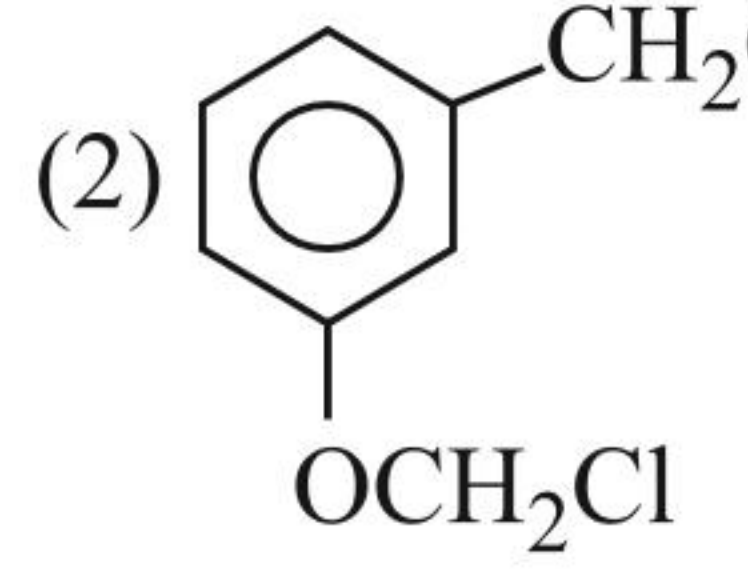
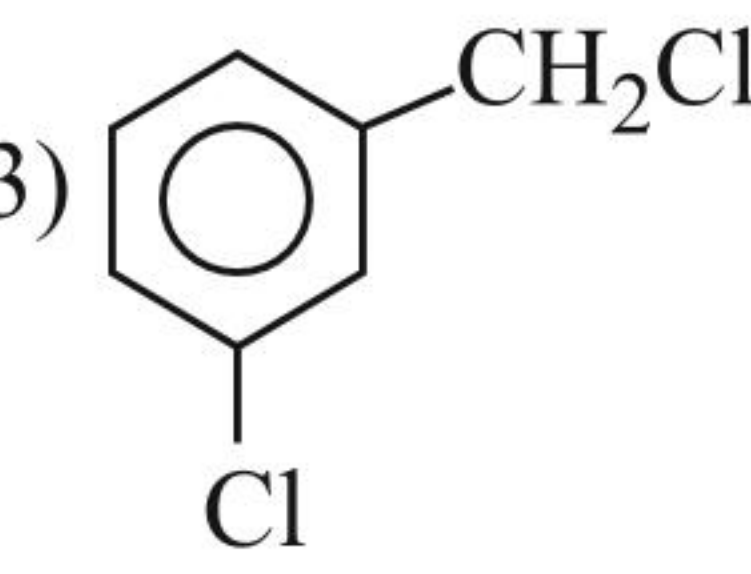
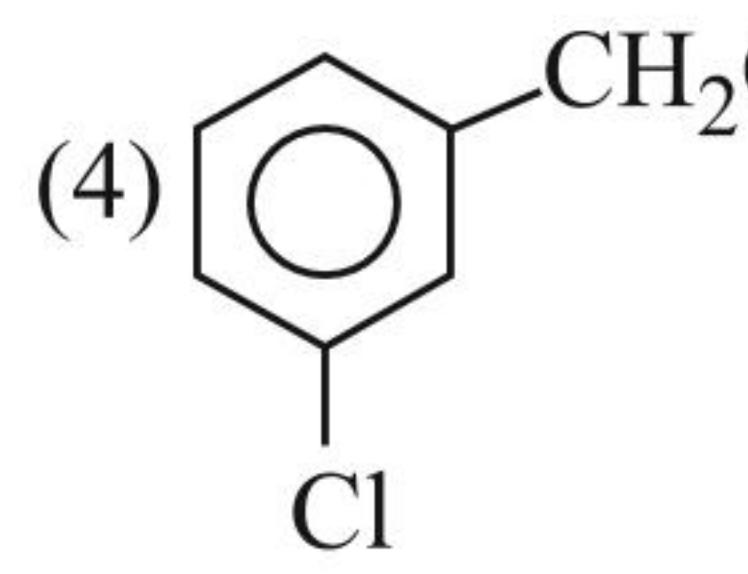
The compound (A) is:

- (1)  (2) 
(3)  (4) None

123. Which of the following would work best for the synthesis of the ether shown below?

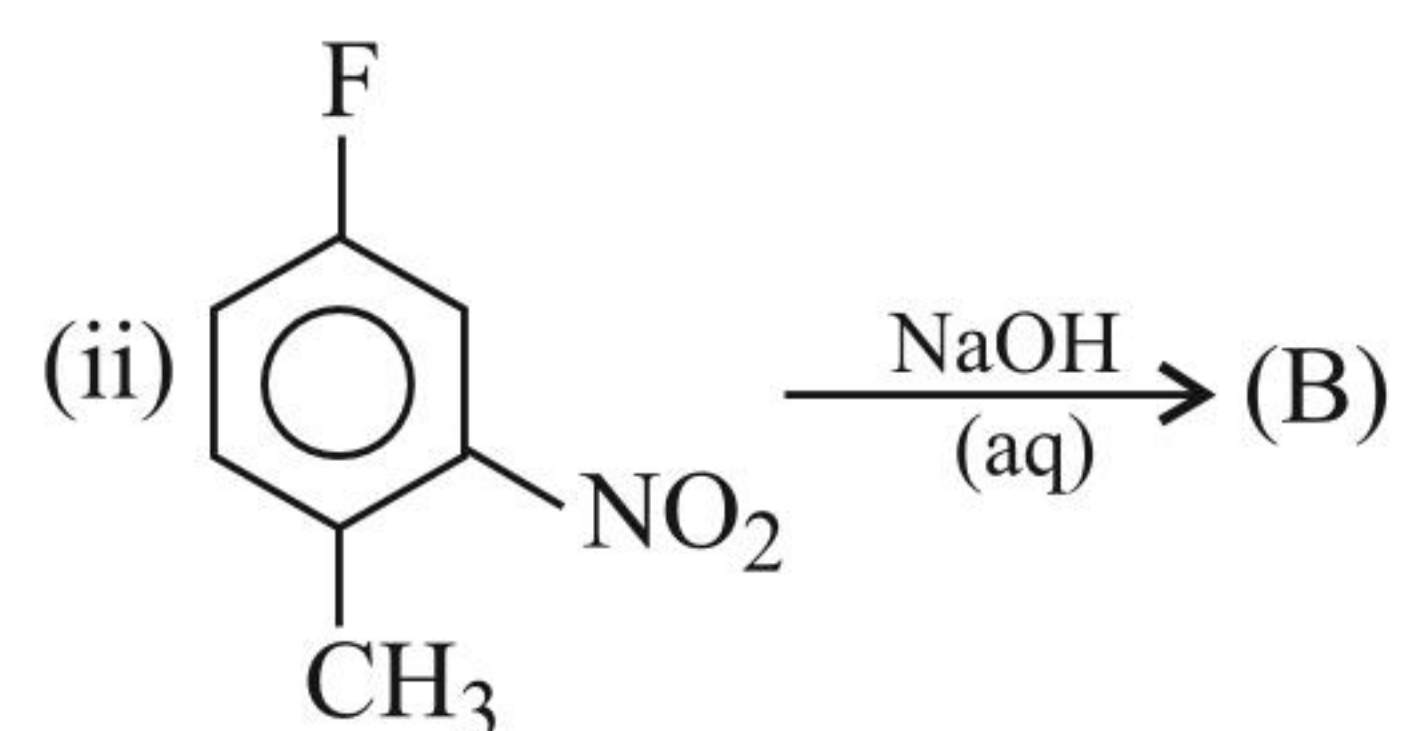
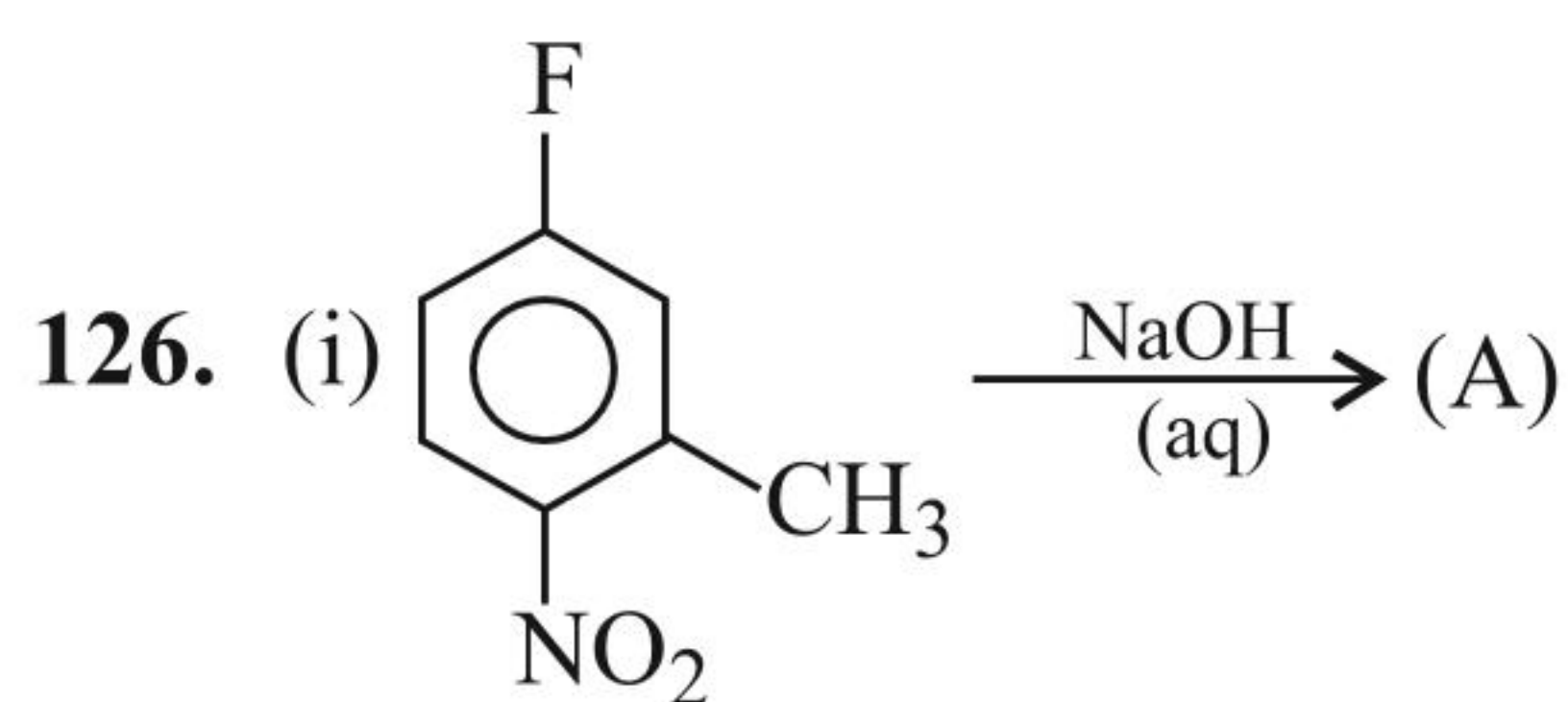
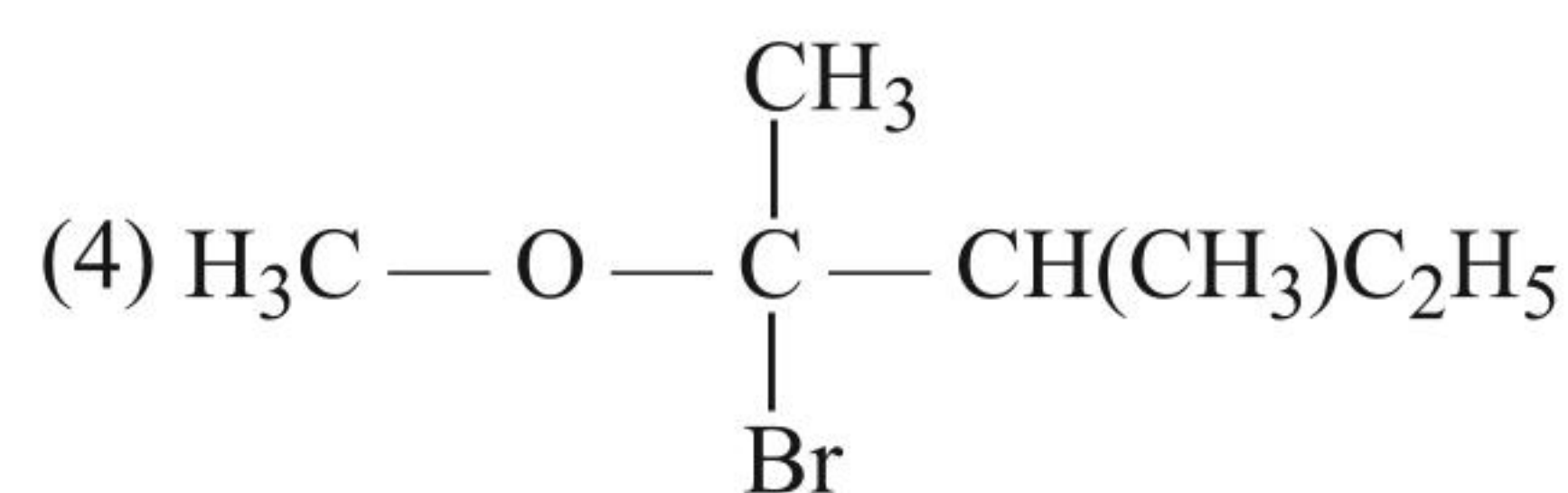
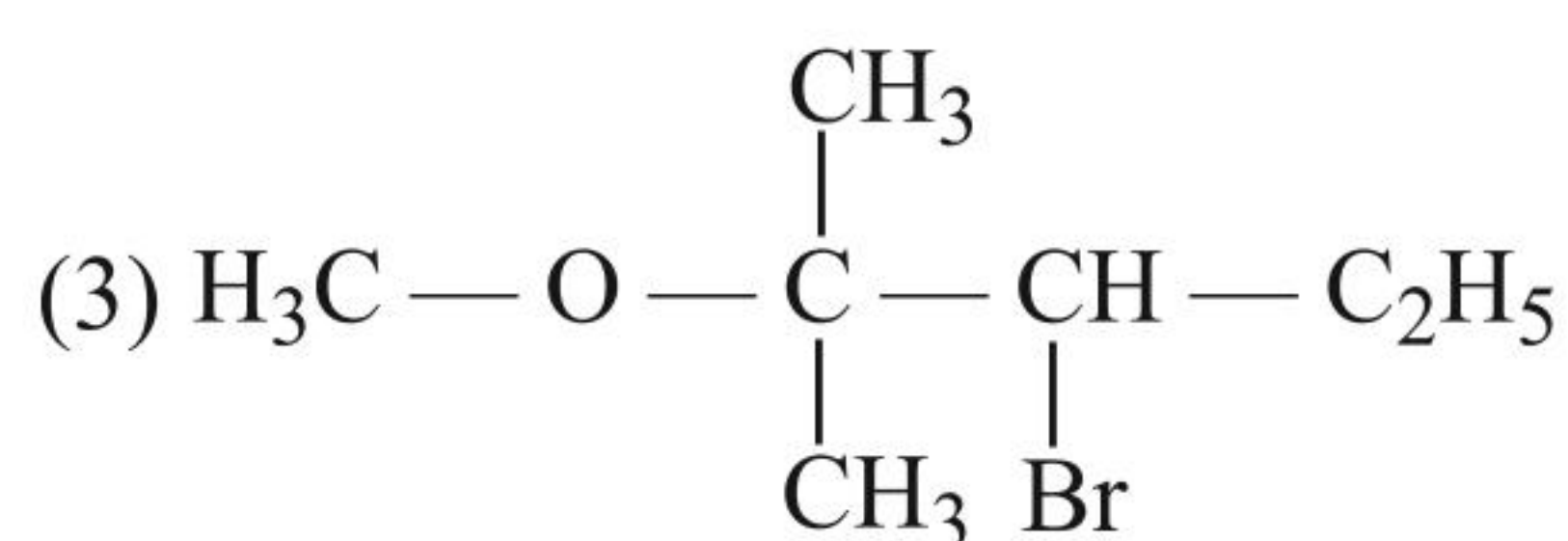
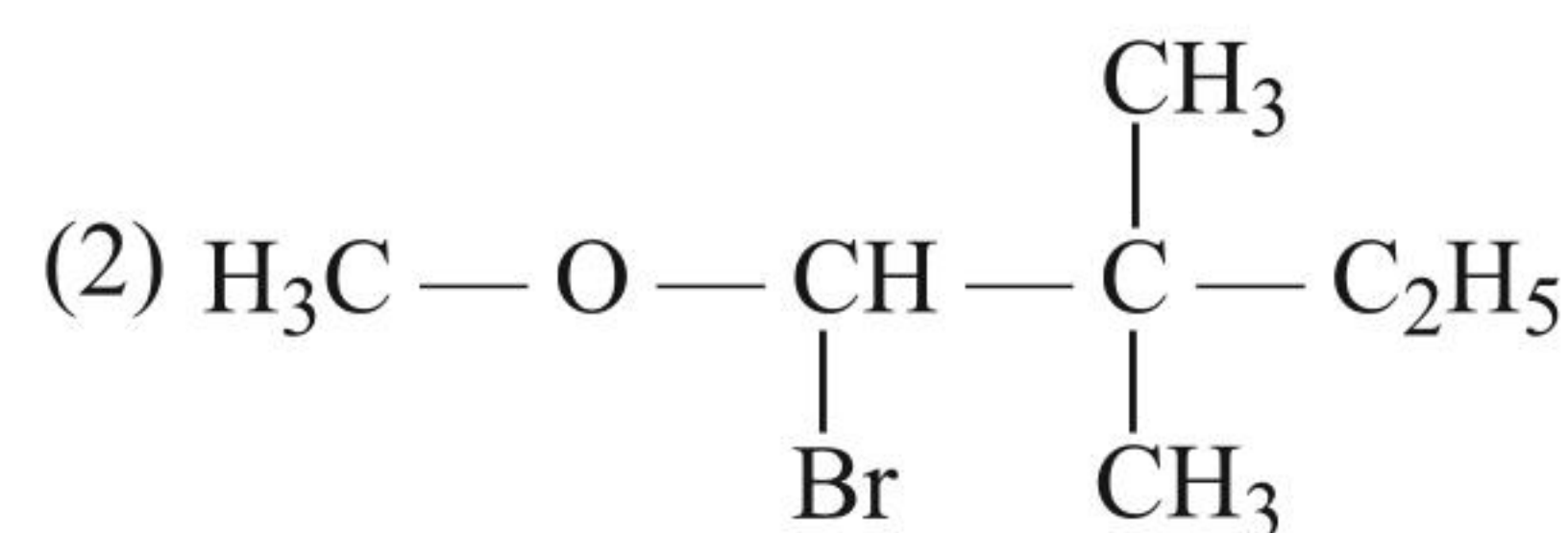
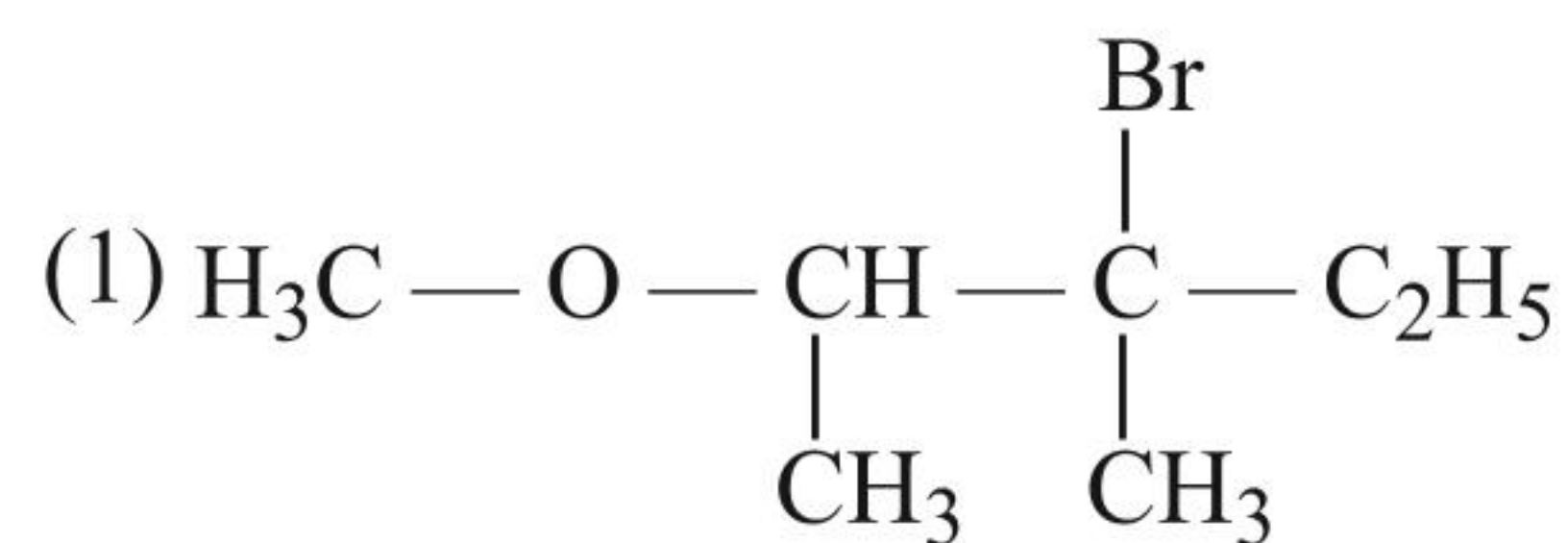
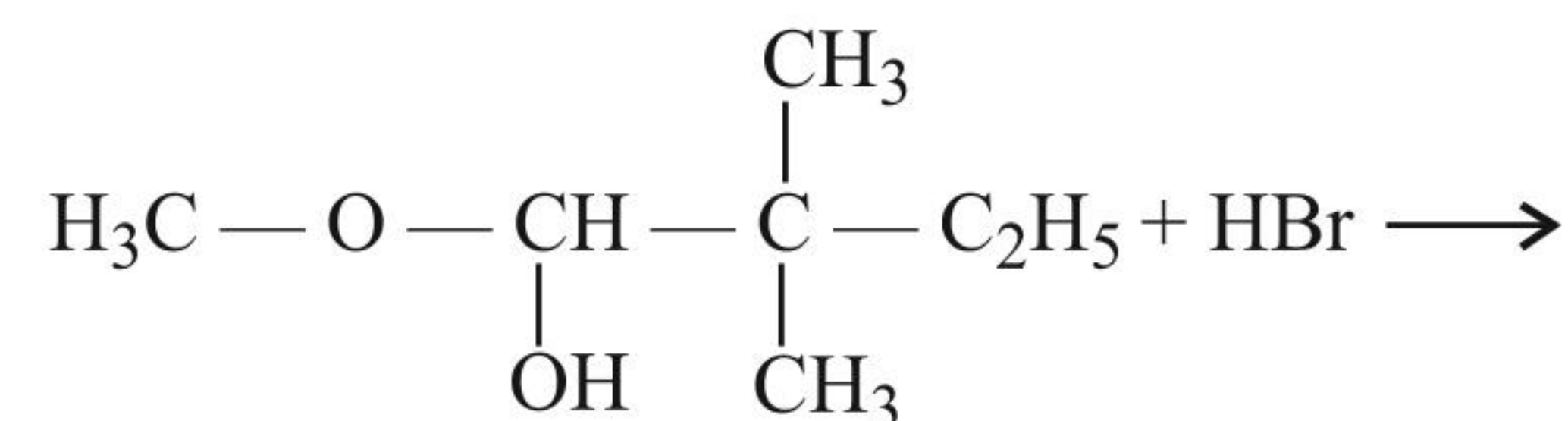


The product A in the above reaction is:

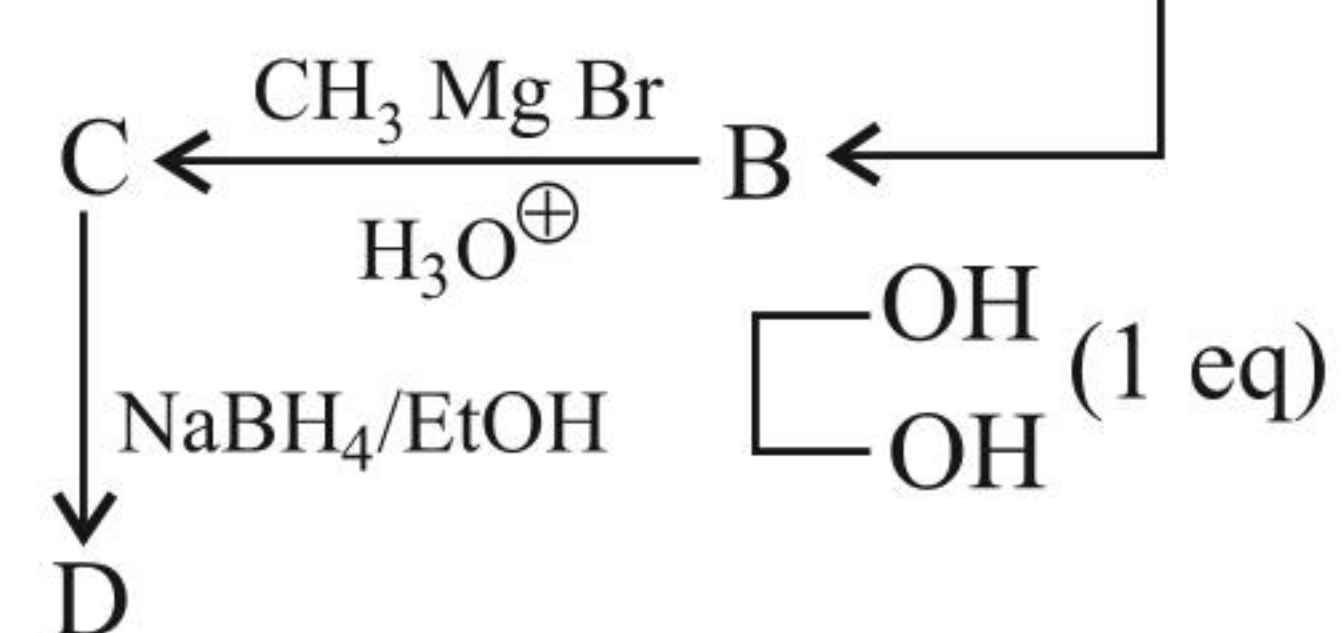
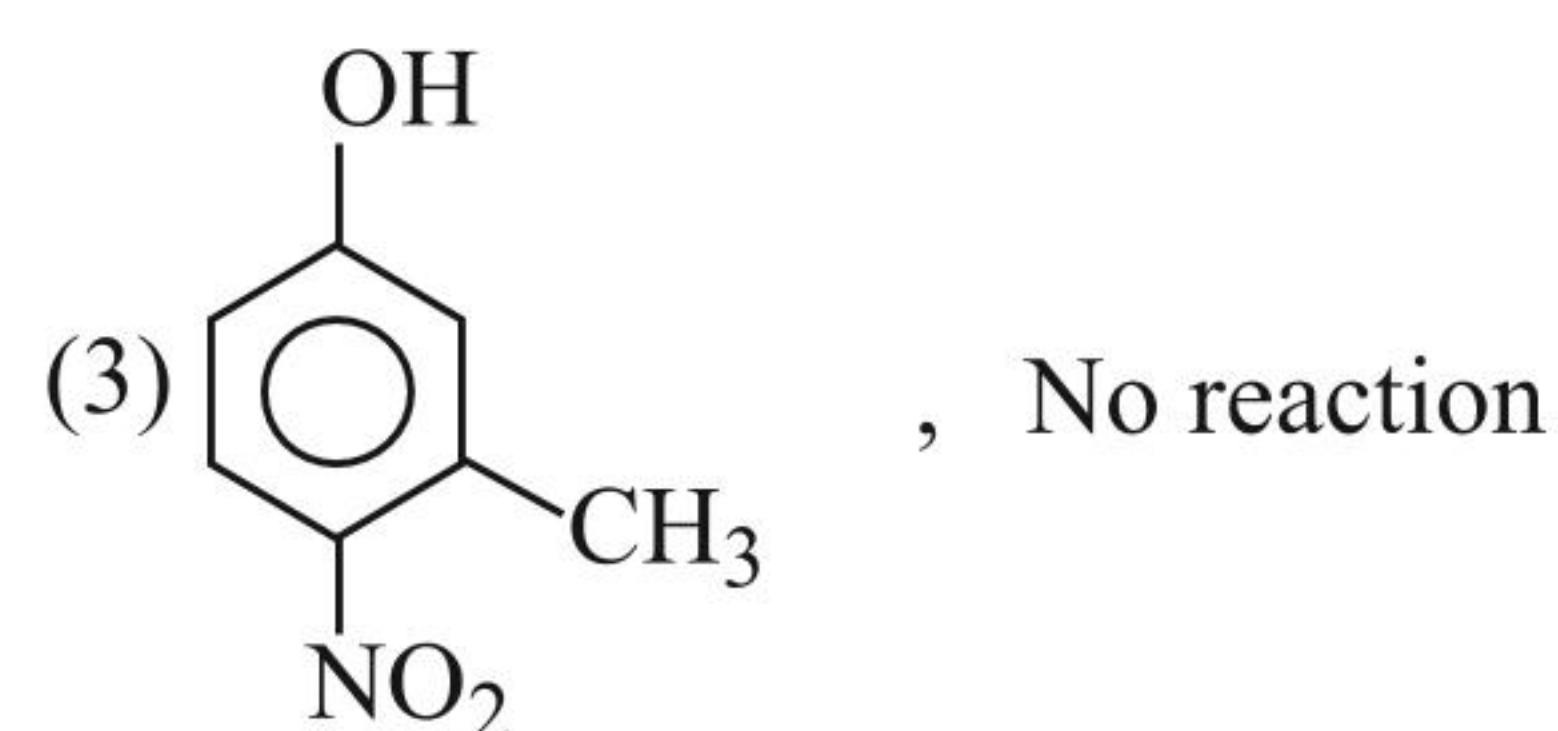
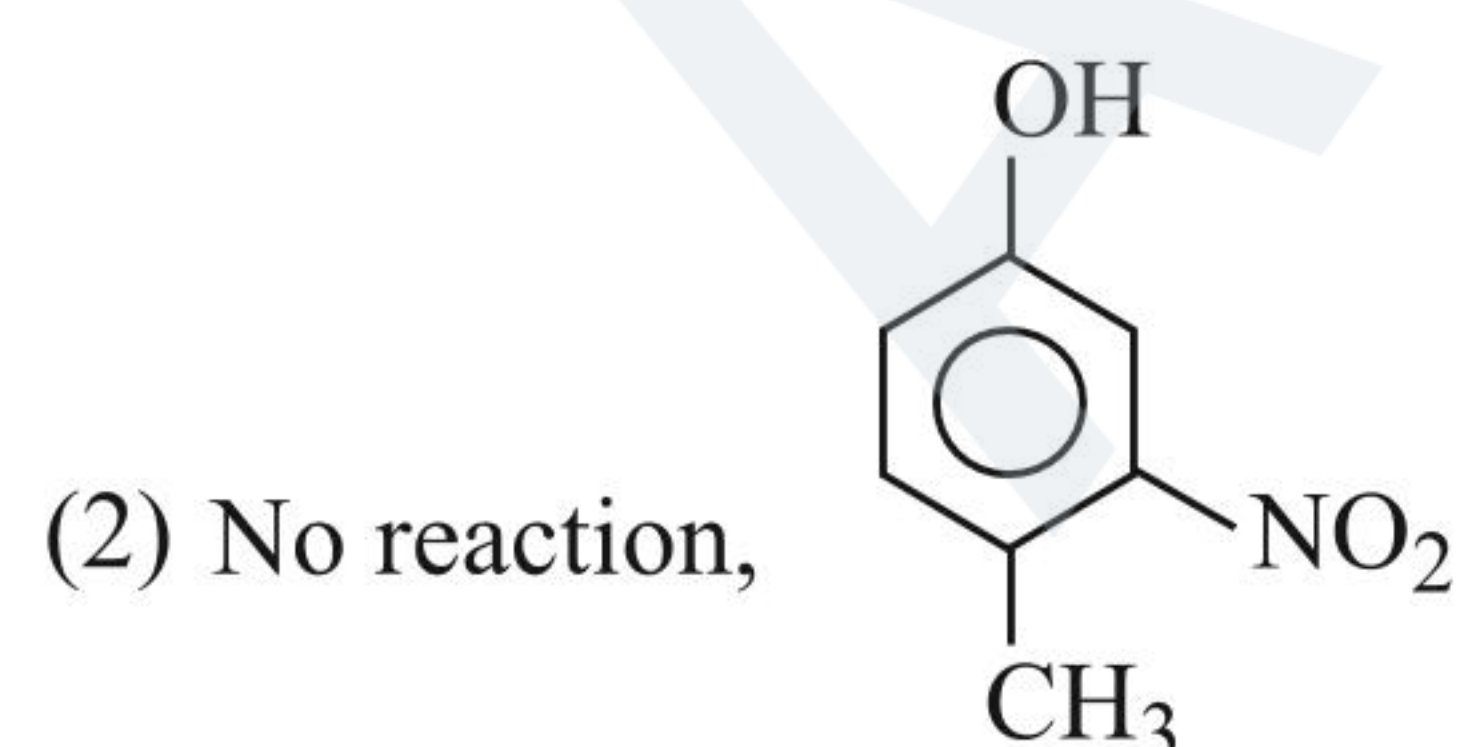
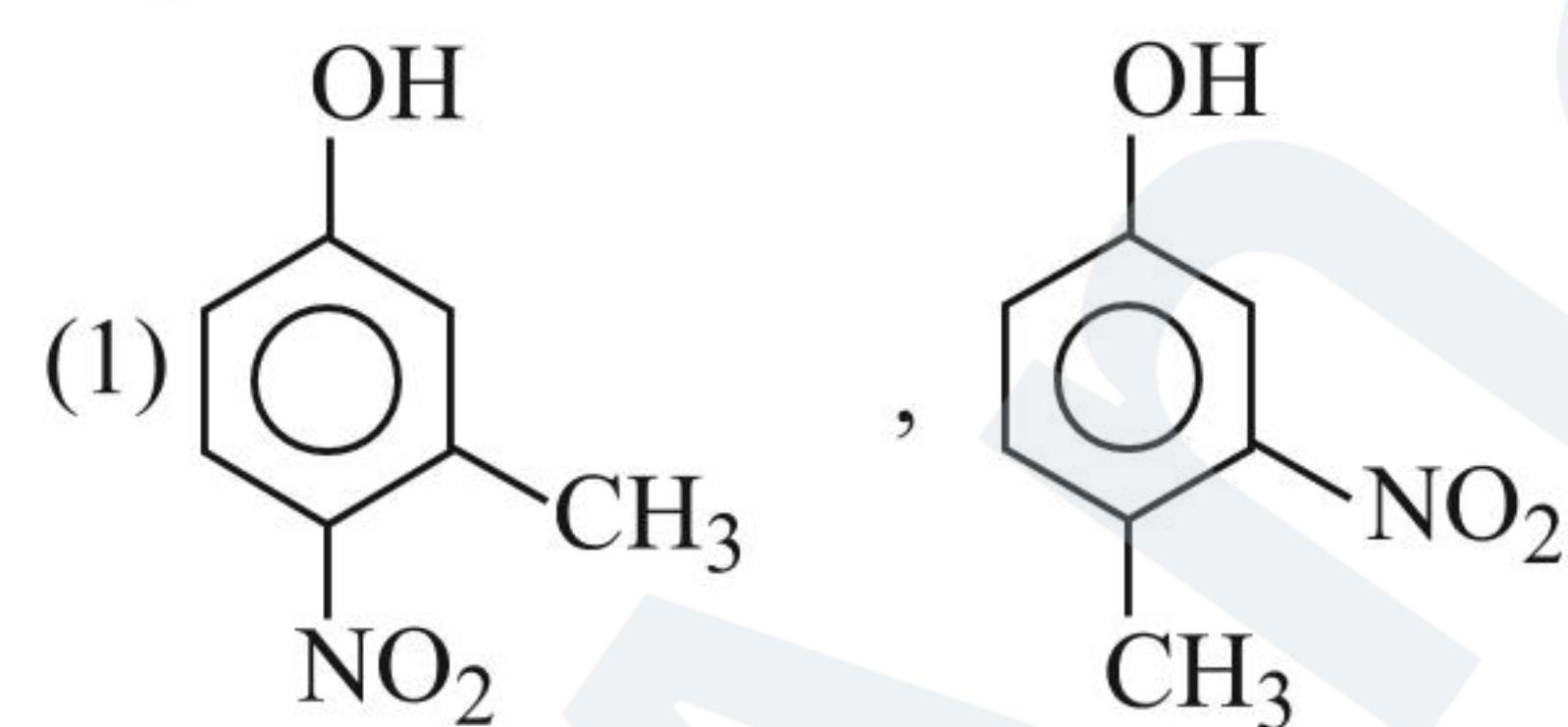
- (1)  (2) 
(3)  (4) 

Miscellaneous

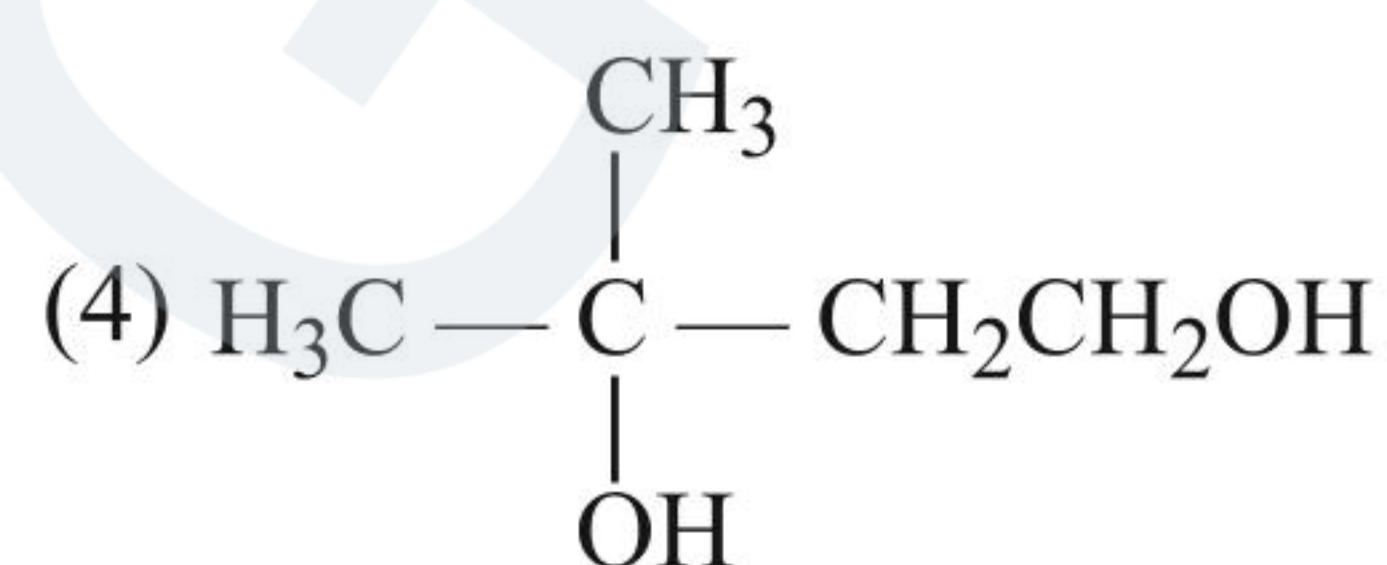
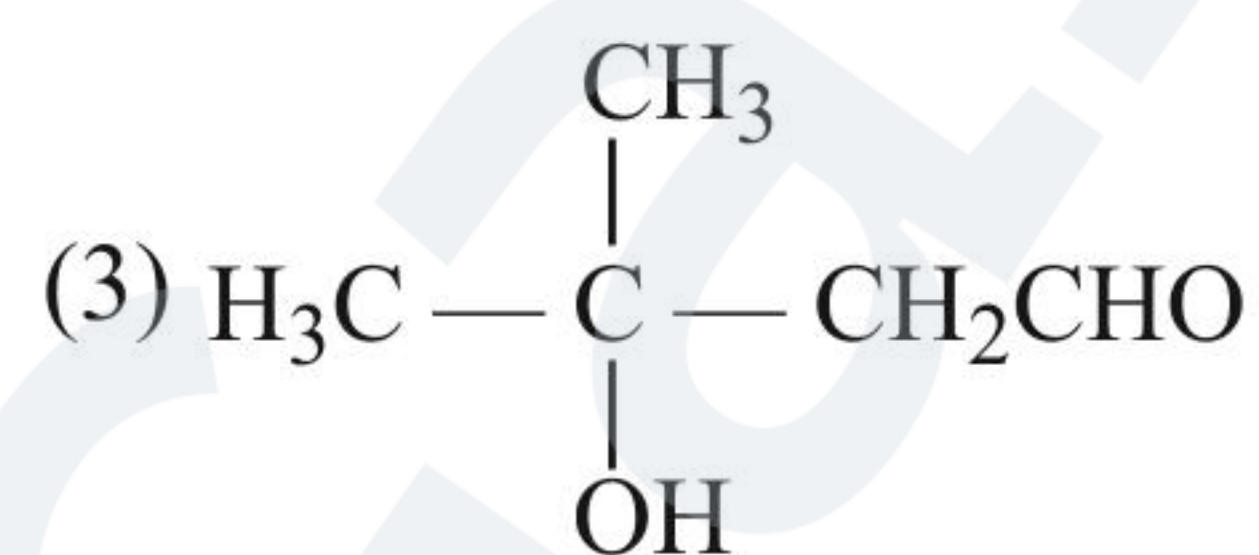
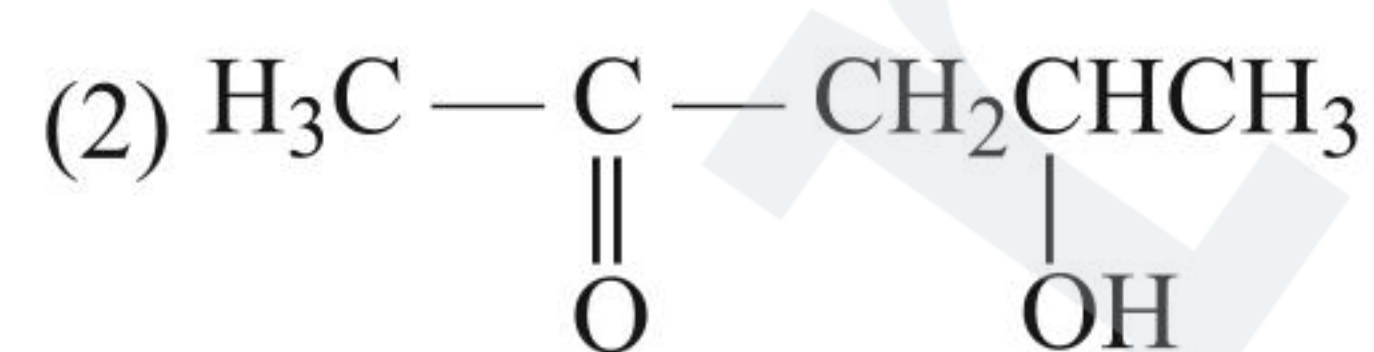
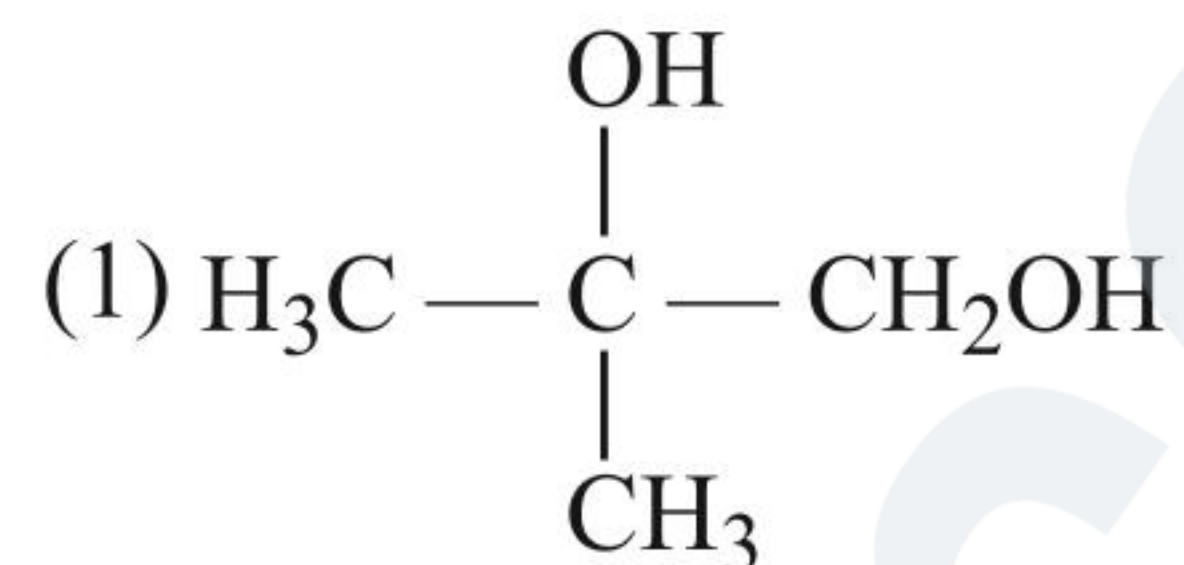
125. Major product formed in following reaction is:



Products (A) & (B) respectively (at moderate conditions) are:



Products D in above reaction is:

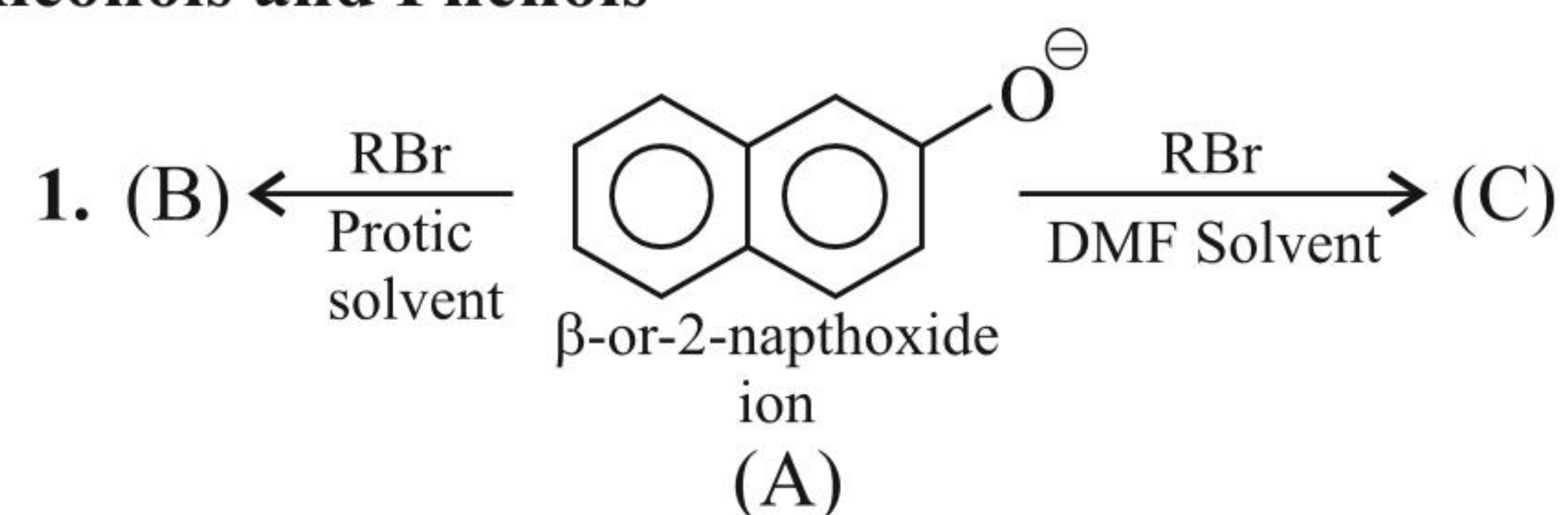


128. Select the incorrect statement?

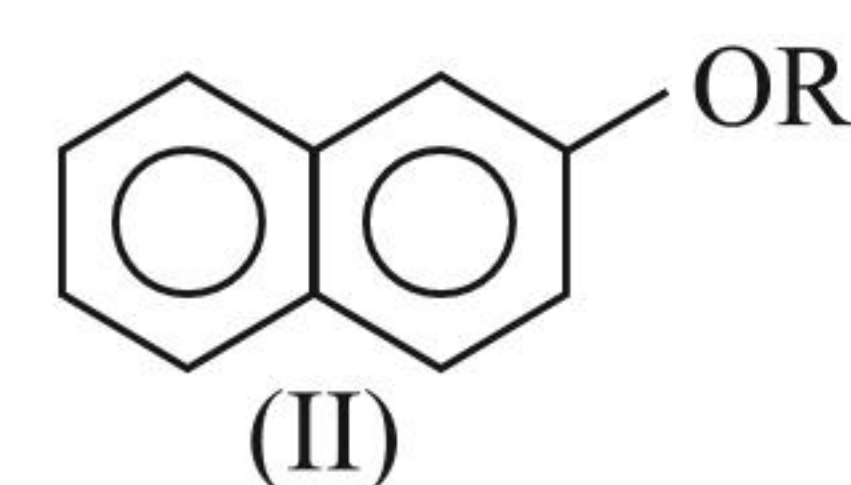
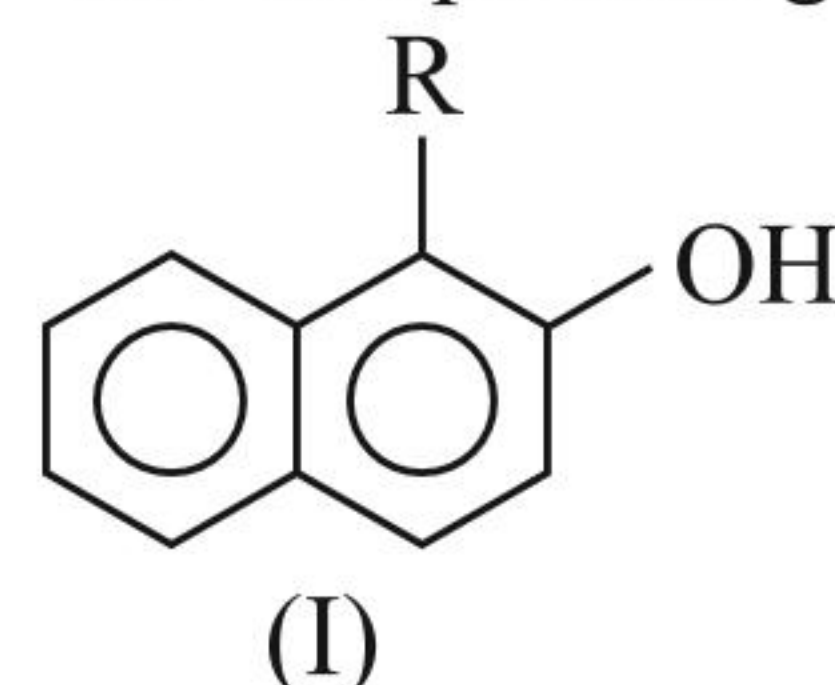
- (1) Phenols are oxidised in air to dark coloured mixtures.
- (2) Reimer-Tiemann reaction is example of electrophilic substitution reaction.
- (3) Lucas test is used to identify 1°, 2° and 3° alcohols.
- (4) *o*-Methylphenol is more acidic than phenol due to ortho effect.

Multiple Correct Answers Type

Alcohols and Phenols

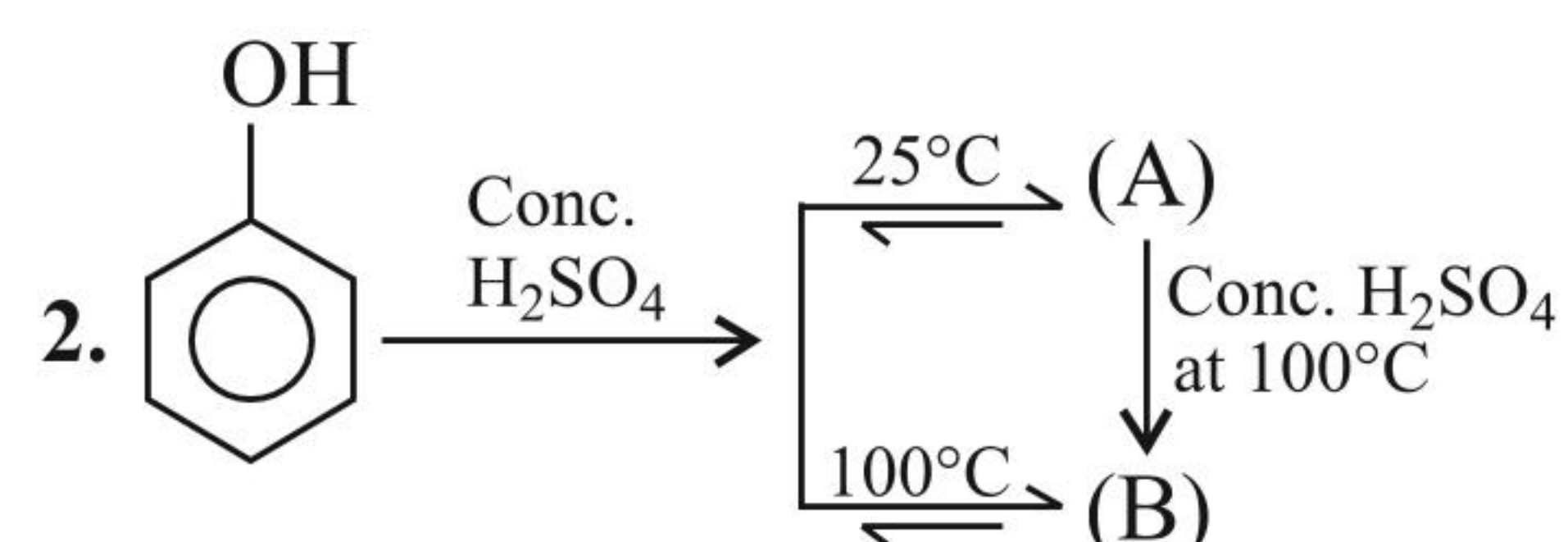


The compounds given are:

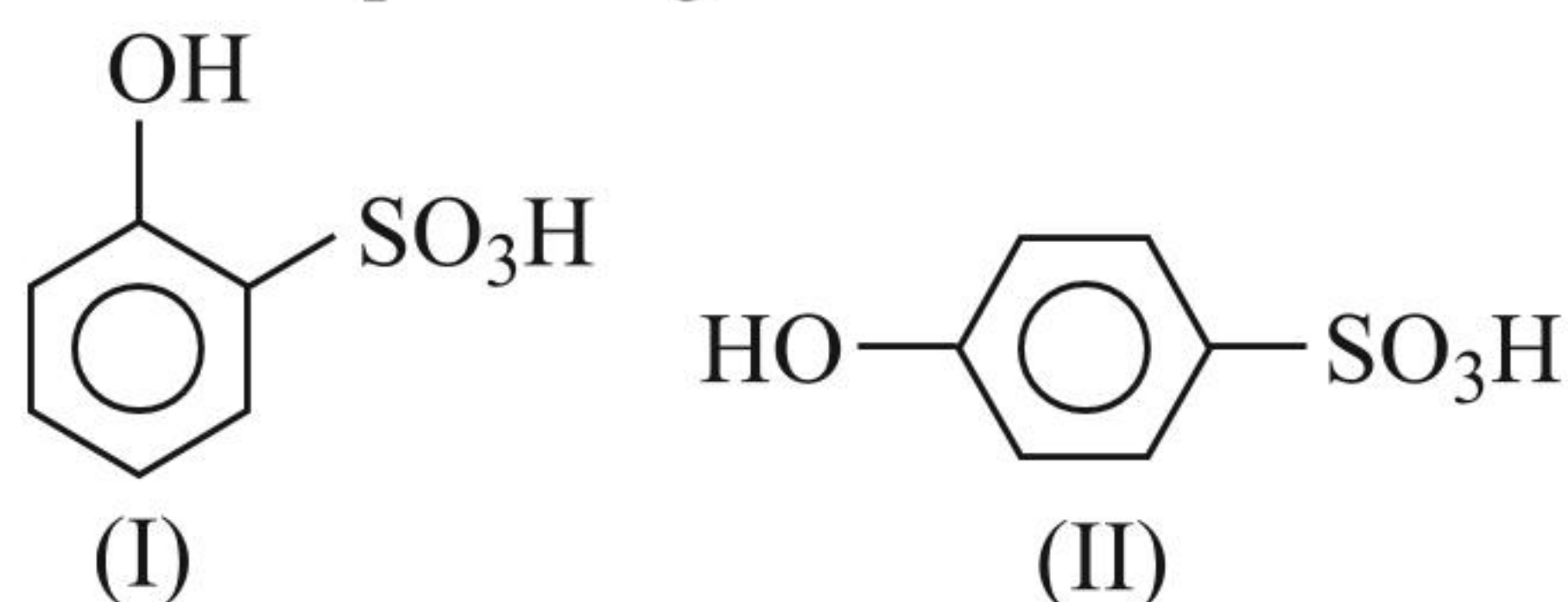


Which of the following statements is/are correct?

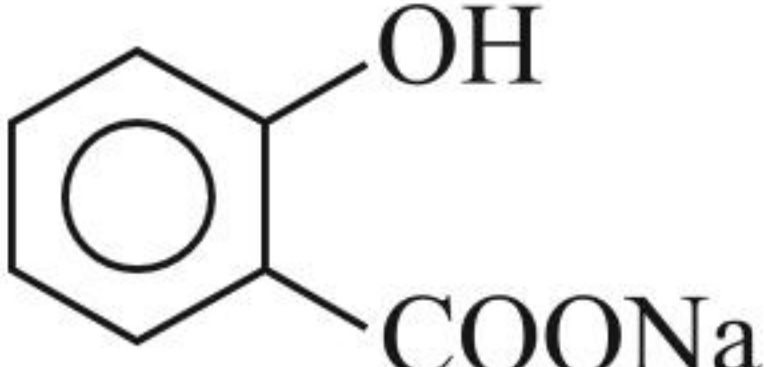
- (1) The compound (B) is (I).
- (2) The compound (B) is (II).
- (3) The compound (C) is (I).
- (4) The compound (D) is II.

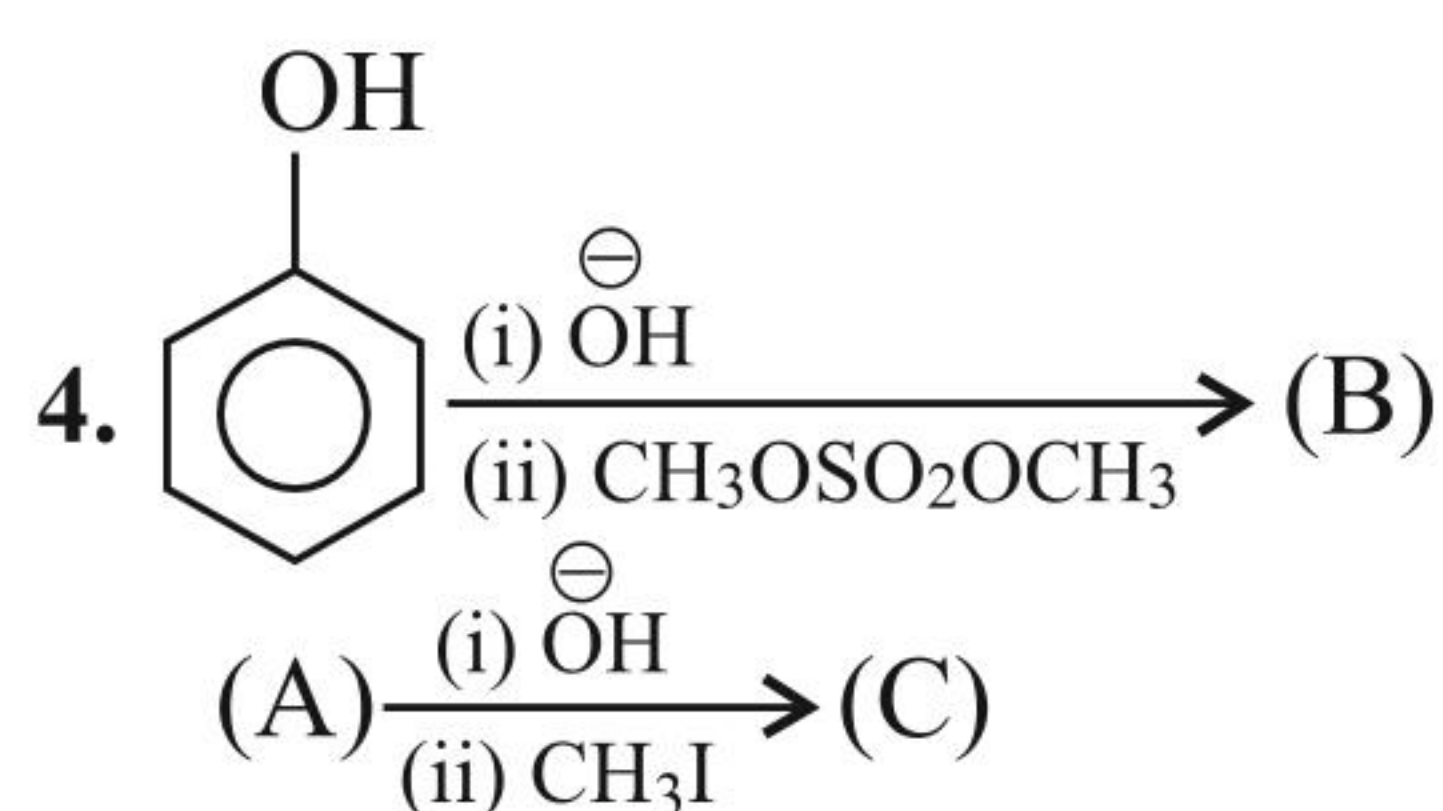


The compounds given are:



Which of the following statements is/are correct?

- (1) Compounds (A) and (B) are (I) and (II), respectively.
 - (2) Compound (I) is the major product at lower temperature when the reaction is under kinetic or rate control.
 - (3) Compound (II) is the major product at high temperature when the reaction is under thermo-dynamical or equilibrium control.
 - (4) Compound (II) is more stable.
3. Which of the following acid-base reactions is/are feasible?
- (1) $\text{PhONa} + \text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{PhOH} + \text{CH}_3\text{CH}_2\text{ONa}$
 - (2) $\text{PhOH} + \text{NaOH} \longrightarrow \text{PhONa} + \text{H}_2\text{O}$
 - (3) $\text{PhONa} + \text{aq. HCl} \longrightarrow \text{PhOH} + \text{NaCl}$
 - (4) $\text{PhONa} + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow$ 



The products (B) and (C), respectively, are:

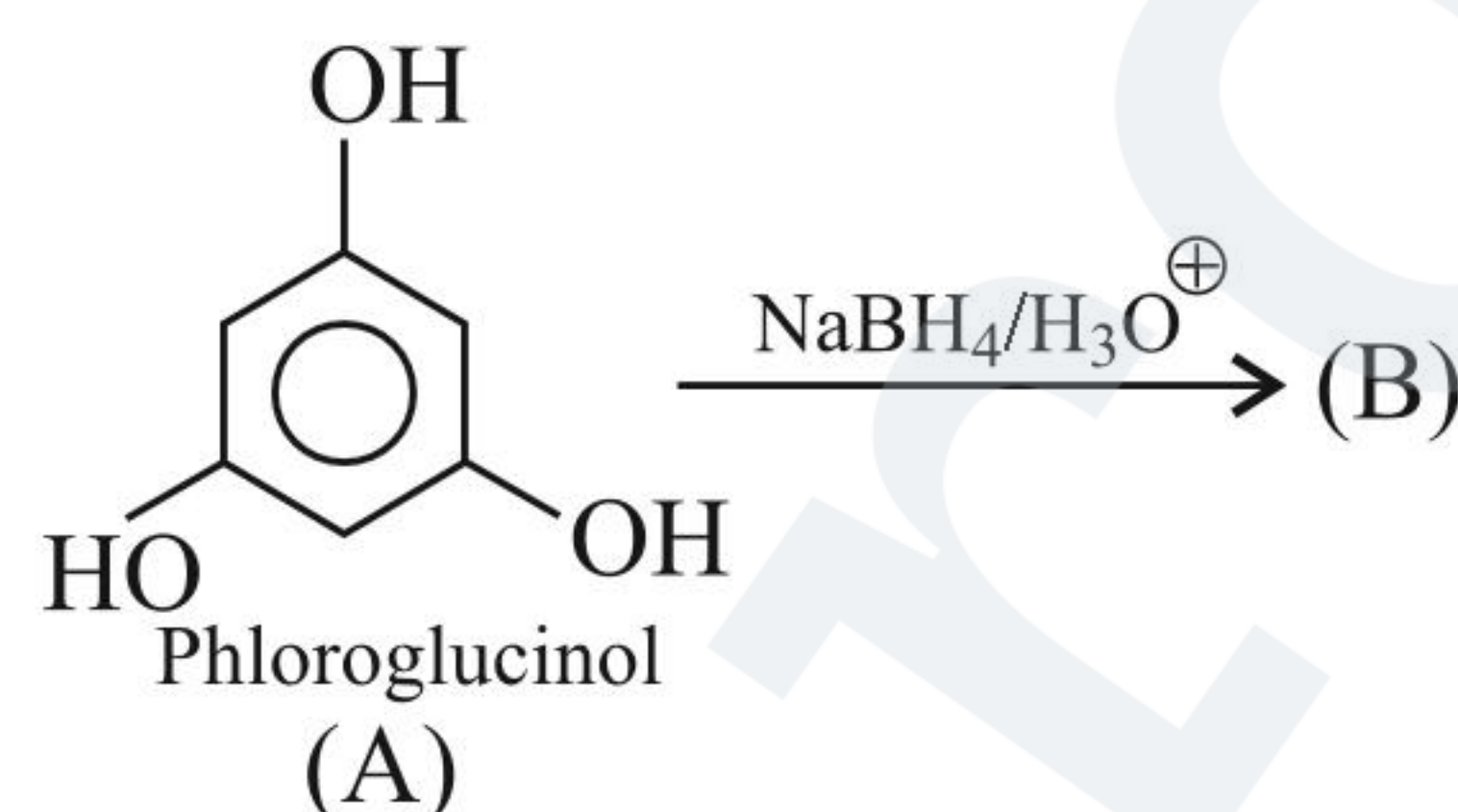
- (1) Both (B) and (C) are PhOCH_3
- (2) (B) is $\text{Ph} - \text{O} - \text{S}(=\text{O})_2 - \text{OCH}_3$
- (3) (B) is $\text{Ph} - \text{O} - \text{S}(=\text{O})_2 - \text{CH}_3$
- (4) (B) is both (2) and (3)

5. Which of the following statements is/are correct?
- (1) 4-Chlorophenol (I) will dissolve in NaOH but 4-chloro-1-methyl benzene (II) will not.
 - (2) 4-Methyl benzoic (III) acid will dissolve in aq. NaHCO_3 but 4-methyl phenol (IV) will not.
 - (3) 2,4,6-Trinitrophenol (V) will dissolve in aq. NaHCO_3 but 4-methyl phenol (VI) will not.
 - (4) 4-Ethyl phenol (VII) will dissolve in aq. NaOH but ethyl phenyl ether (VII) will not.
6. Which of the following statements is/are correct?
- (1) Phenyl vinyl ether (I) will decolourise Br_2/CCl_4 solution but ethyl phenyl ether (II) will not.
 - (2) 4-Fluorophenol (III) is a stronger acid than 4-methyl phenol (IV).

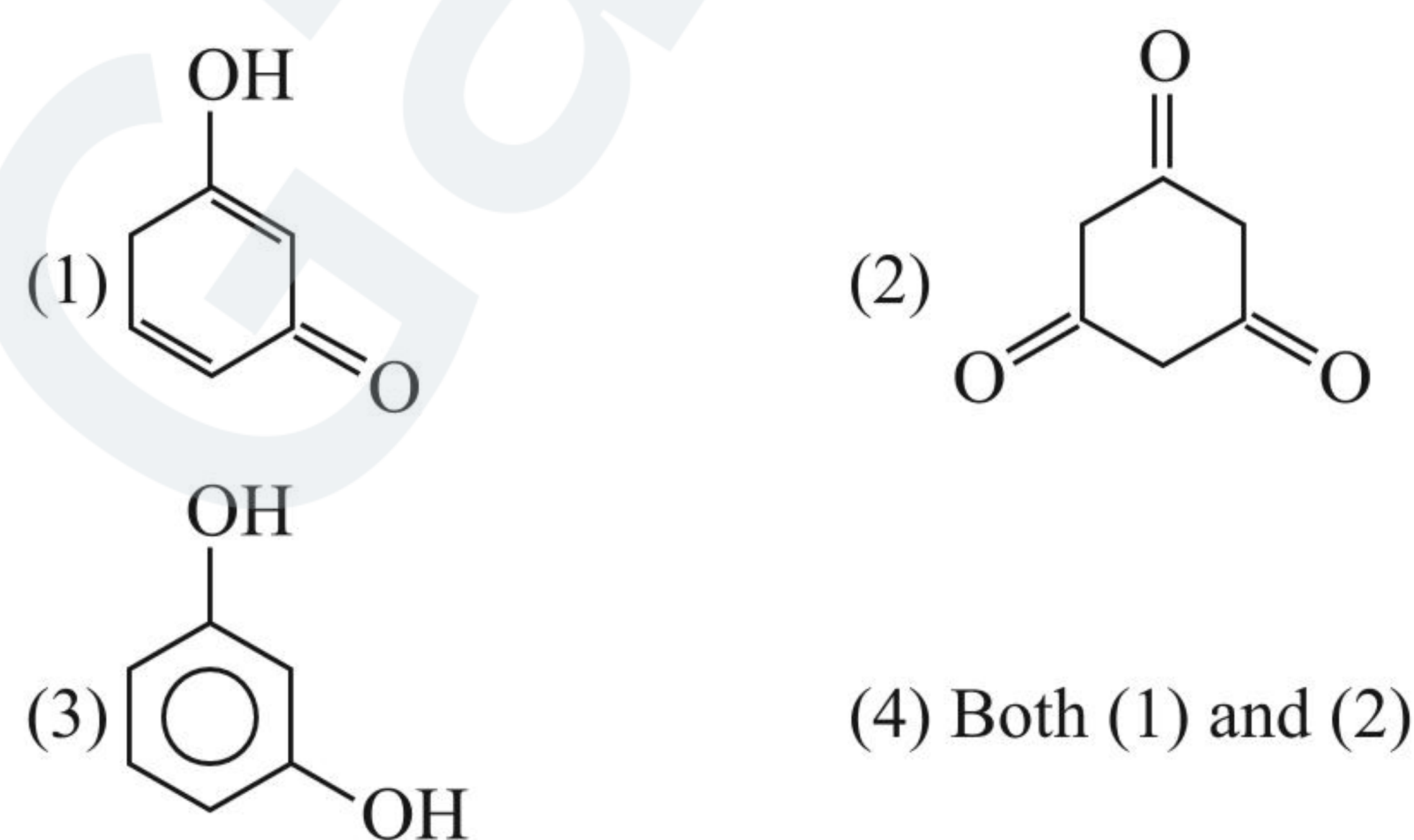
(3) 3-Nitrophenol (V) is a stronger acid than 4-nitro-phenol (VI).

(4) 4-Chlorophenol (VII) is a stronger acid than 4-fluorophenol (VIII).

7. Phenols are generally not changed with $\text{NaBH}_4/\text{H}_3\text{O}^+$ 1,3- and 1,4-benzenediols and 1,3,5-benzenetriols are unchanged under these conditions. However, 1,3,5-benzenetriol (phloroglucinol) gives a high yield of product (B).

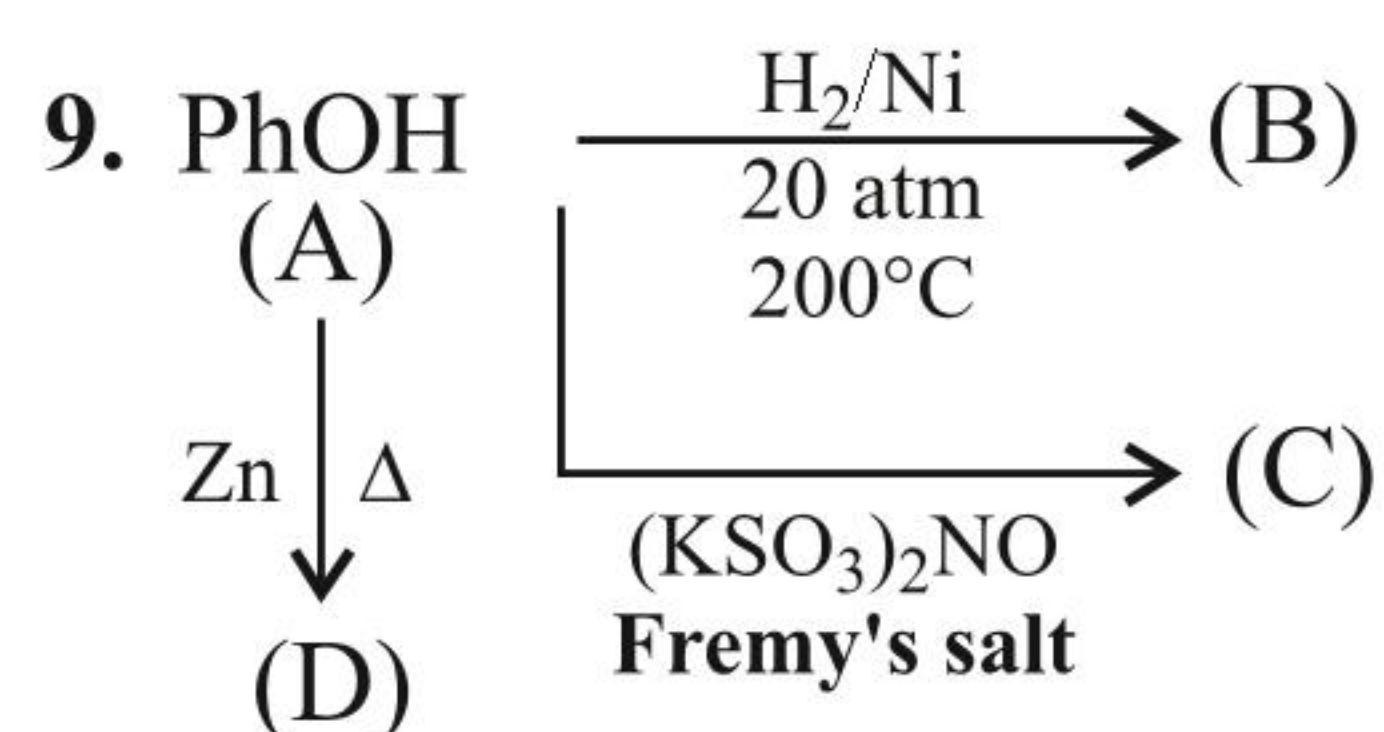


The Compound (B) is:



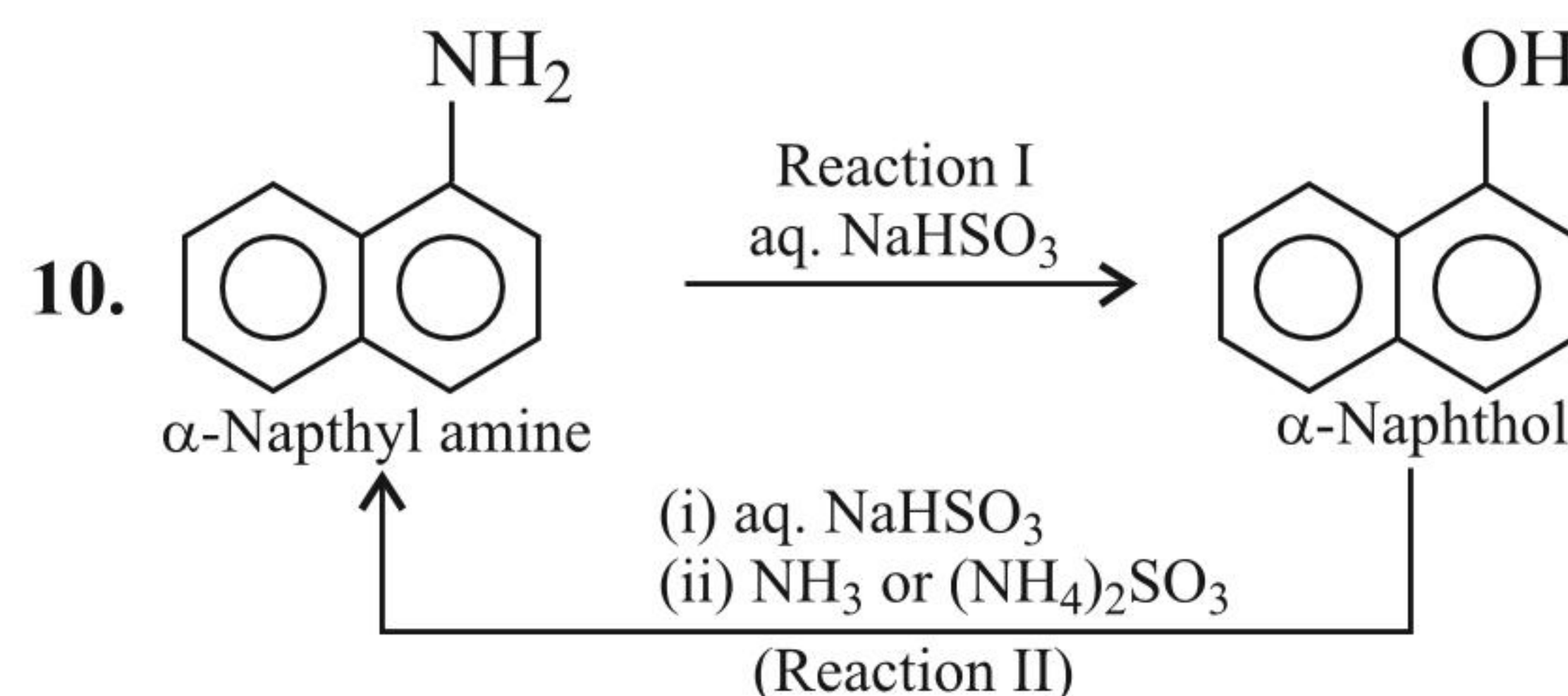
The product(s) are:

- (1) Butyl propyl ether
- (2) Dipropyl ether
- (3) Dibutyl ether
- (4) Propene + But-2-ene (*cis* and *trans*) + Butene



The compounds (B), (C), (D), respectively, are:

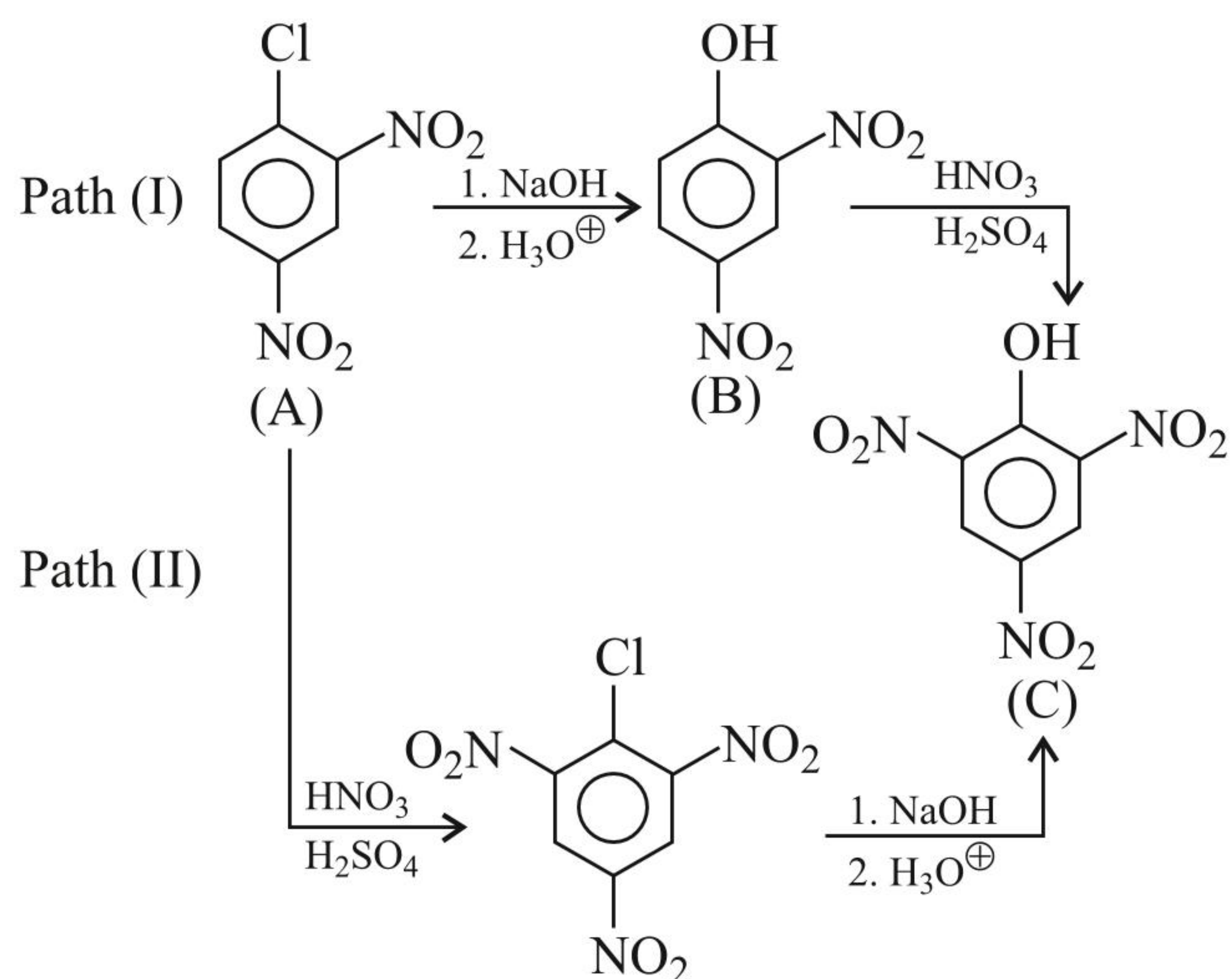
- (1) Cyclohexanol, benzene, and *p*-quinone
- (2) Benzene, cyclohexanol, and *p*-quinone
- (3) *p*-Quinone, cyclohexanol, and benzene
- (4) Cyclohexanol, *p*-quinone, and benzene



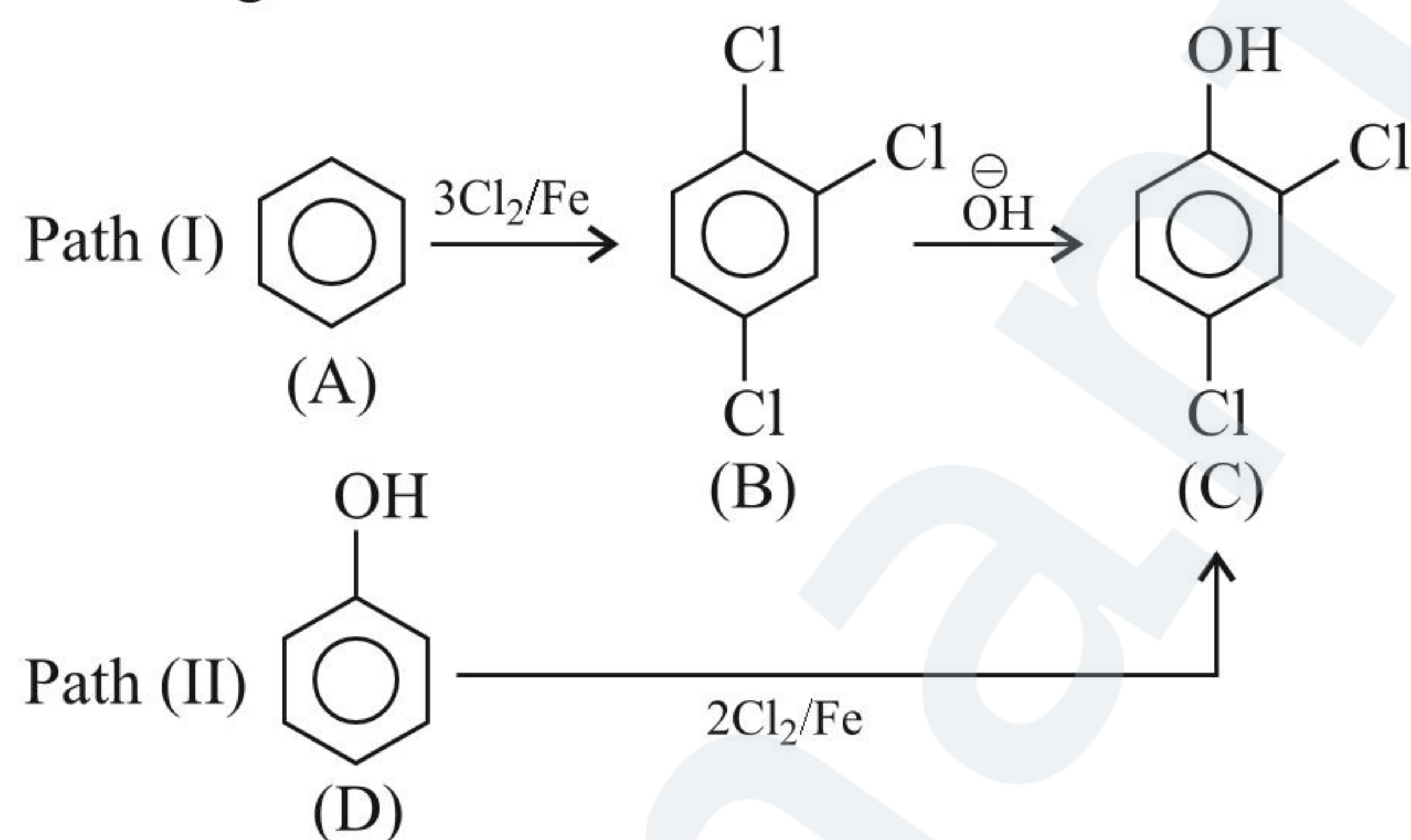
Reactions I and II are limited mainly to naphthalene compounds. These reactions are called, respectively:

- (1) Bucherer reaction and its reversal.
- (2) Bischler–Napieralski reaction and its reversal.
- (3) Birnbaum–Simonini reaction and its reversal.
- (4) Borodine–Hunsdiecker reaction and its reversal.

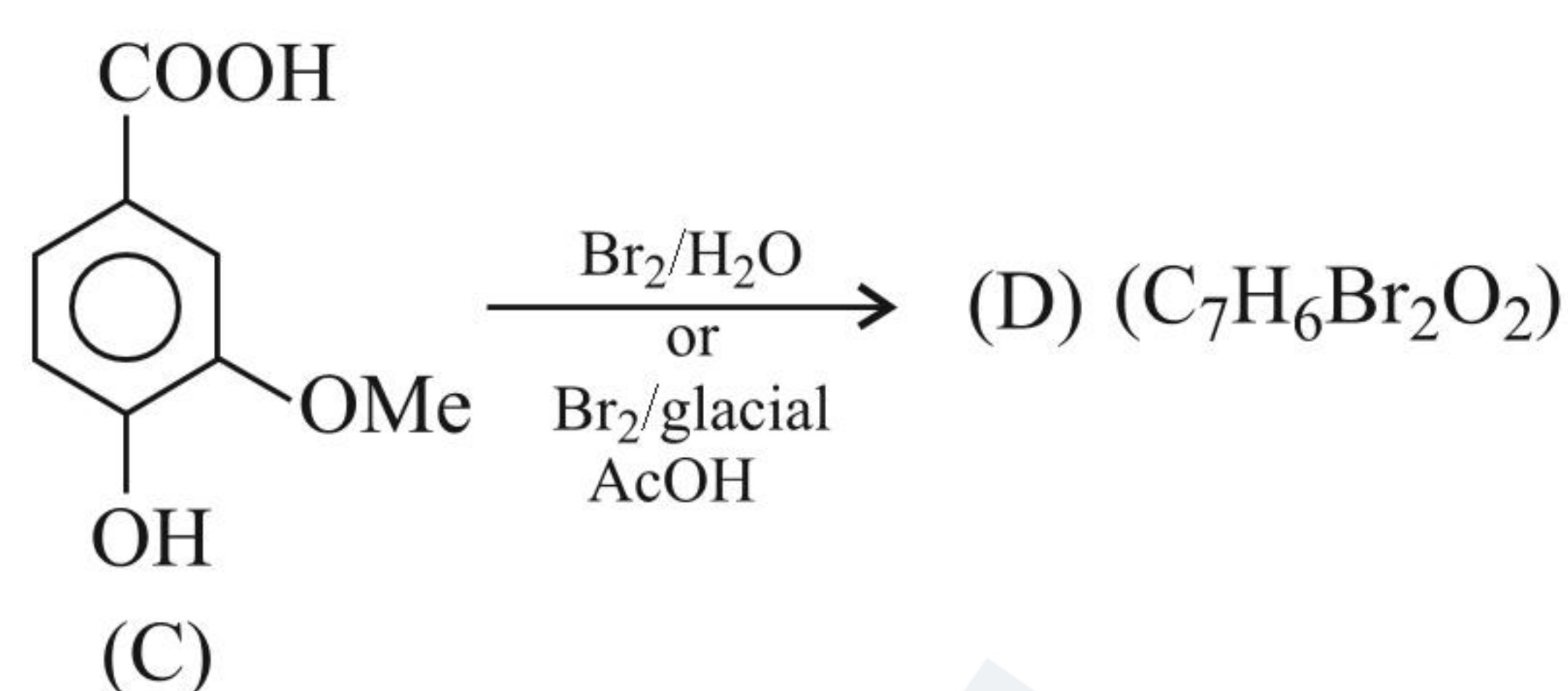
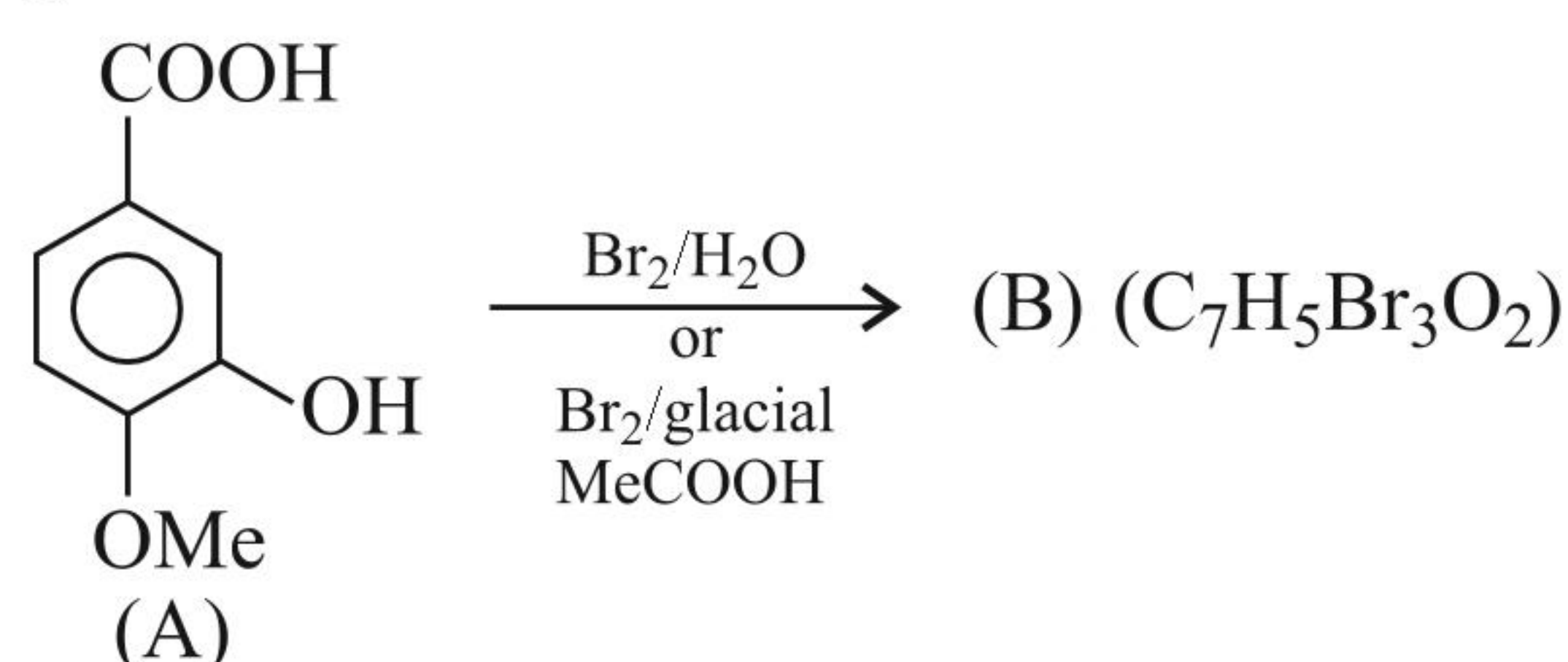
11. Which of the following statements is/are correct about the following reactions?



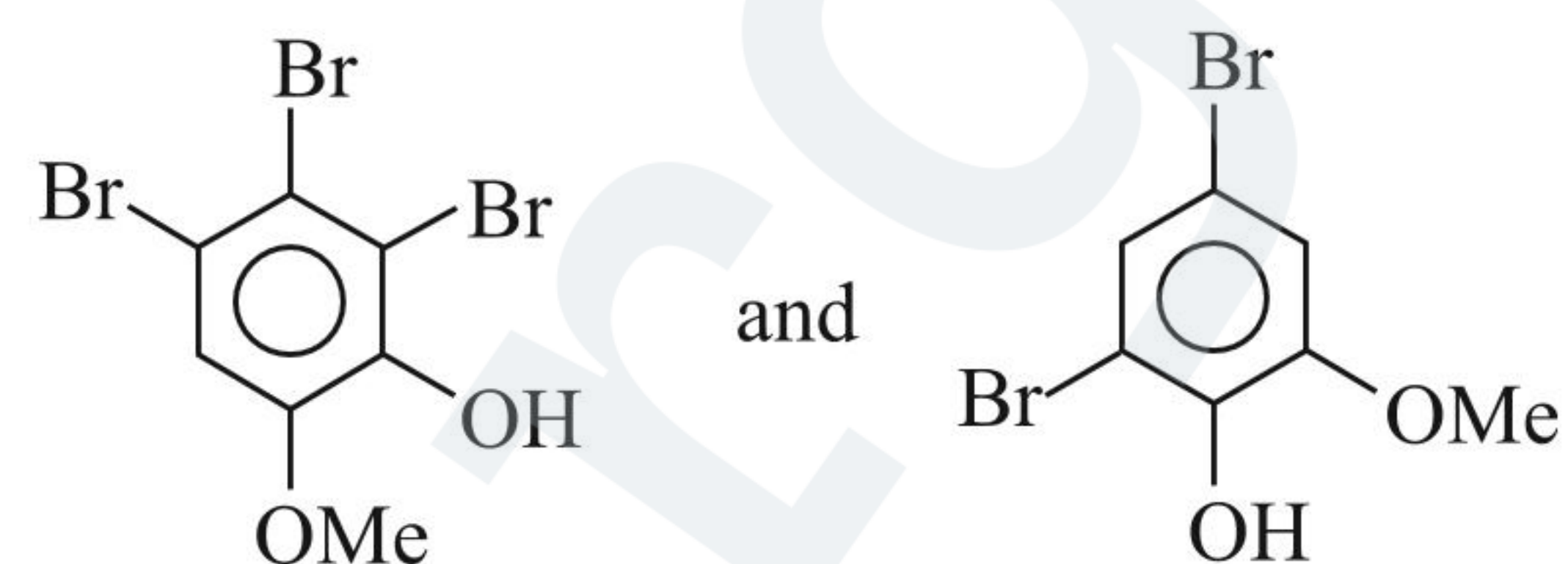
- (1) Path I is feasible.
 - (2) Path II is feasible.
 - (3) (A) cannot be nitrated because Cl and two NO₂ atoms deactivate the ring towards further SE reaction.
 - (4) 2,4-Dinitrophenol can be nitrated because the two deactivating NO₂ groups prevent ring oxidation.
12. Which of the following statements is/are correct about the following reactions?



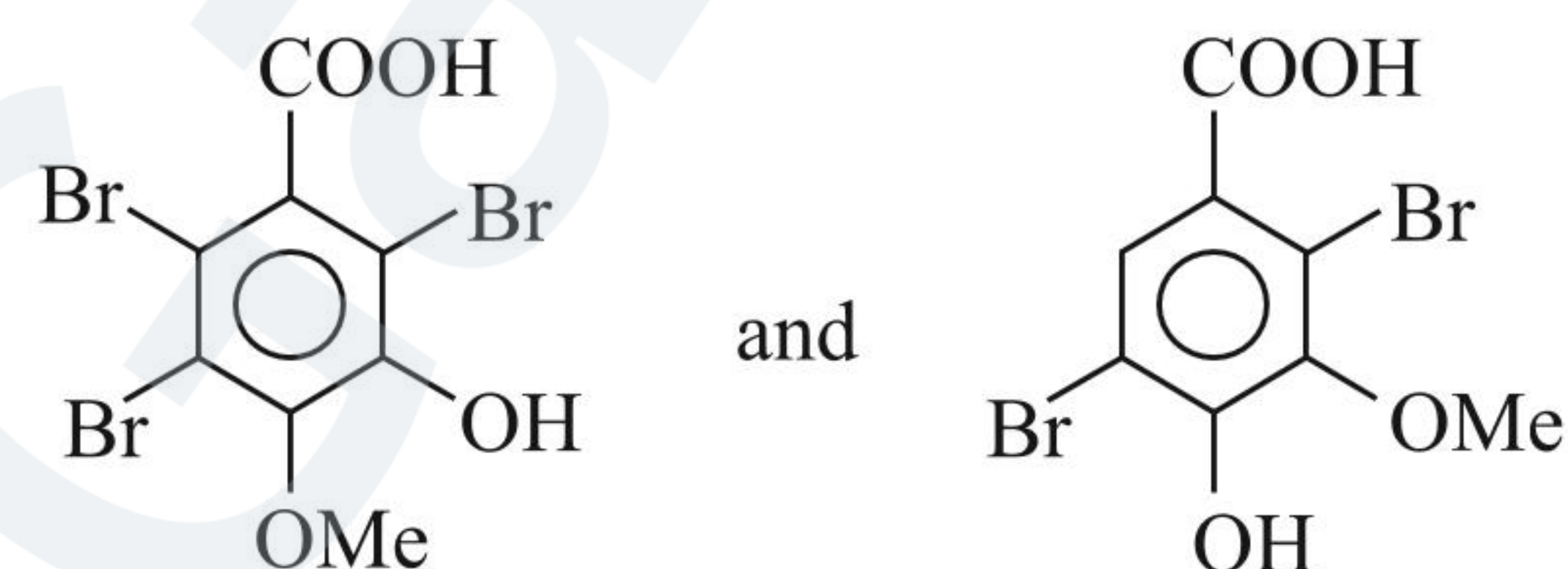
- (1) Both paths I and II are feasible.
 - (2) Path I is feasible.
 - (3) Phenol cannot be chlorinated because the ring is susceptible to oxidation by Cl₂.
 - (4) The formation of (C) from (B) proceeds by ArSN reaction (addition–elimination).
13. Which of the following statements is/are correct about the given reaction?



(1) The products (B) and (D), respectively, are:



(2) The products (B) and (D), respectively, are:



- (3) In the formation of both products (B) and (D), one Br is obtained by ipso substitution while the other Br is obtained by SE reaction.
 - (4) In the formation of (B) and (D), two Br atoms are obtained by ipso substitution, whereas the other Br is obtained by SE reaction.
14. Which of the following statements is/are correct?

- (1) The nitration of phenol is faster than phenyl acetate.
- (2) The reaction of PhO[⊖] is faster than with PhCH₂Cl.
- (3) Base-catalysed hydrolysis of *p*-nitrophenyl acetate is faster than phenyl acetate.
- (4) Acid-catalysed esterification of PhOH is faster than *p*-nitrophenol with MeCOOH.

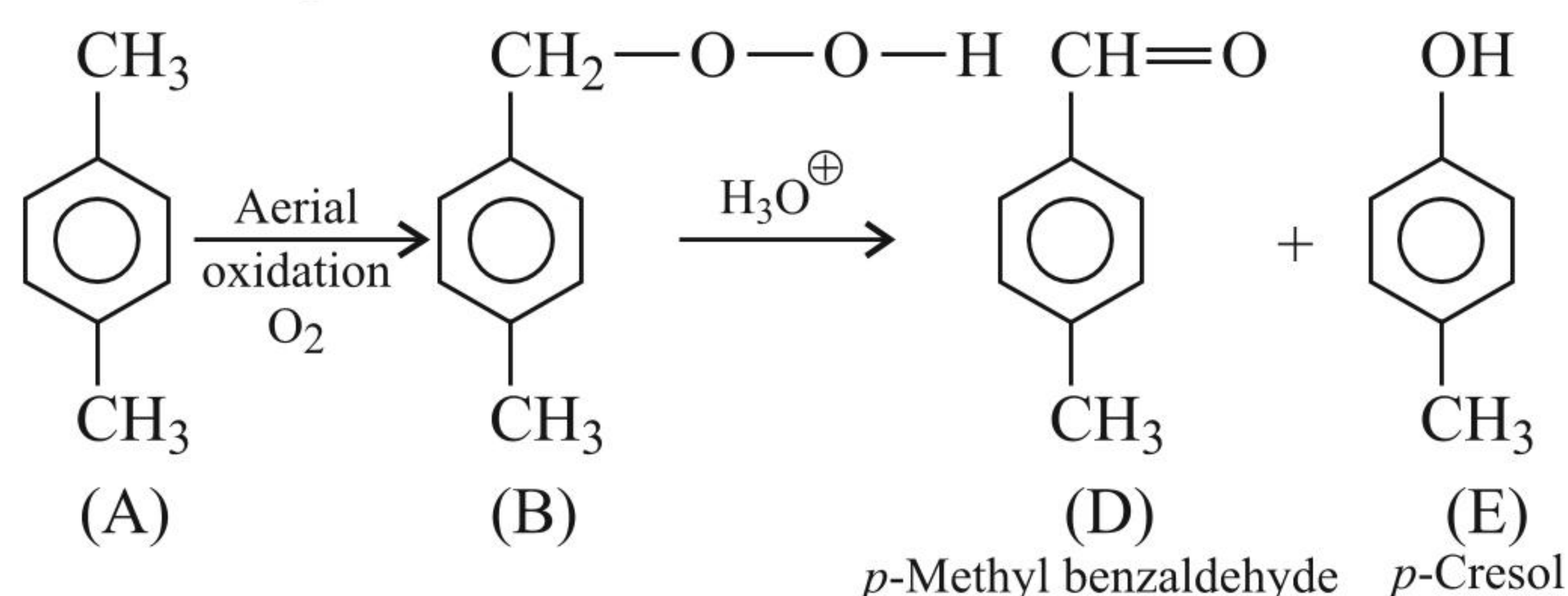
15. Which of the following statements is/are correct?

- (1) PhOH has a higher boiling point than PhSH (benzenethiol).
- (2) *p*-Hydroquinone has a higher melting point than catechol.
- (3) *o*-Nitrophenol has a lower boiling point than *m*- and *p*-isomers.
- (4) *o*-Hydroxybenzaldehyde is more water soluble than *m*- and *p*-isomers.

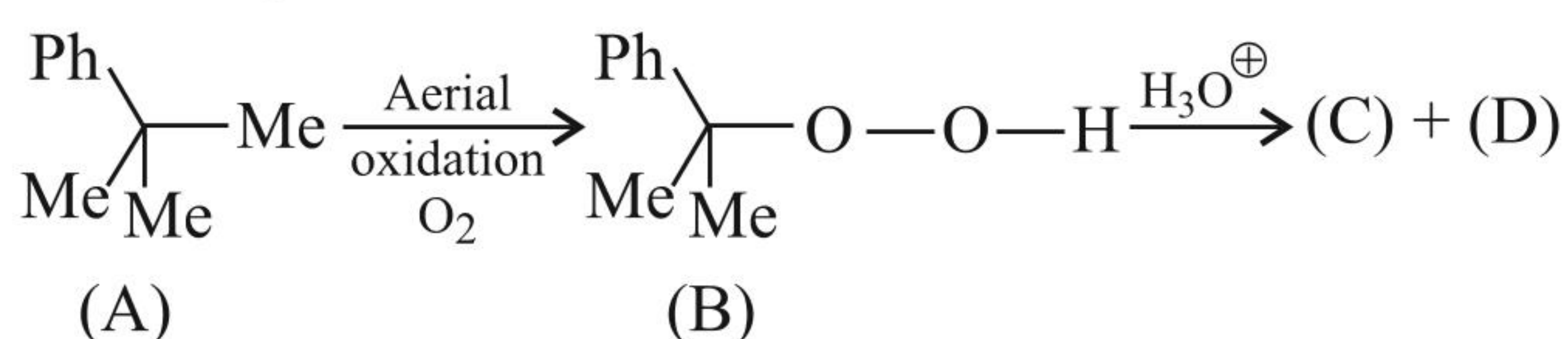
16. Which of the following statements is/are wrong?

- (1) THF (tetrahydrofuran) is a stronger Lewis base than diethyl ether.
- (2) Diisopropyl ether is a stronger Lewis base than diethyl ether.
- (3) THF is a stronger Lewis base than DHF (dihydro-furan).
- (4) Furan is a stronger Lewis base than DHF.

17. Which of the following statements is/are correct about the following reaction?



- (1) Compound (D) is in major amount (68%) and (E) is in minor (32%).
 (2) Compound (D) is in minor amount (32%) and (E) is in major (68%).
 (3) The aldehyde (D) arises from migration of H, and cresol (E) comes from migration of *p*-tolyl.
 (4) H is a better migrator.
18. Which of the following statements is/are correct about the following reaction?



- (1) The products (C) and (D), respectively, are $\text{PhOH} + \text{Me}_2\text{C=O}$.
 (2) The products (C) and (D), respectively, are $\text{MeOH} + \text{PhC(=O)Me}$.
 (3) Ph group is a better migrator than Me group.
 (4) Me group is a better migrator than Ph group.
19. Which of the following statements is/are correct?
- (1) Phenol is more easily oxidised than benzene.
 (2) Benzaldehyde and PhCl can be distinguished by NaHSO_3 .
 (3) *p*-Cresol and benzoic acid can be distinguished by NaOH.
 (4) Phenol and benzoic acid can be distinguished by adding dry ice in aqueous NaOH solution.

20. Which of the following is/are less acidic than *p*-nitrophenol.

- (1) *o*-Nitrophenol (2) *m*-Nitrophenol
 (3) Phenol (4) *p*-Cresol

21. The (O—H) group in alcohols can be replaced by:

- (1) SOCl_2 (2) Cl_2
 (3) PCl_5 (4) $\text{P} + \text{Cl}_2$

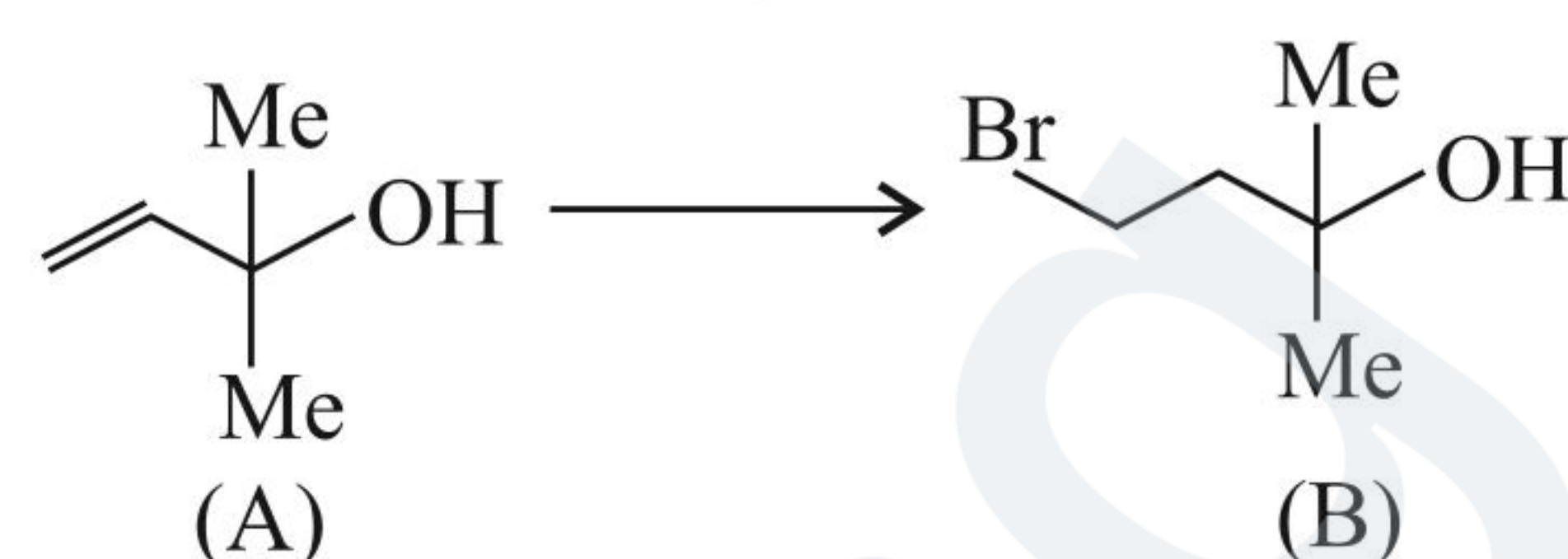
22. Phenol can be prepared by

- (1) Hydrolysis of chlorobenzene with aqueous KOH solution.
 (2) Heating sodium salicylate with ($\text{NaOH} + \text{CaO}$).
 (3) Reacting cumene hydroperoxide with dil. H_2SO_4 .
 (4) Heating benzenediazonium chloride with dil. H_2SO_4 .

23. Esters on reaction with EtMgBr give:

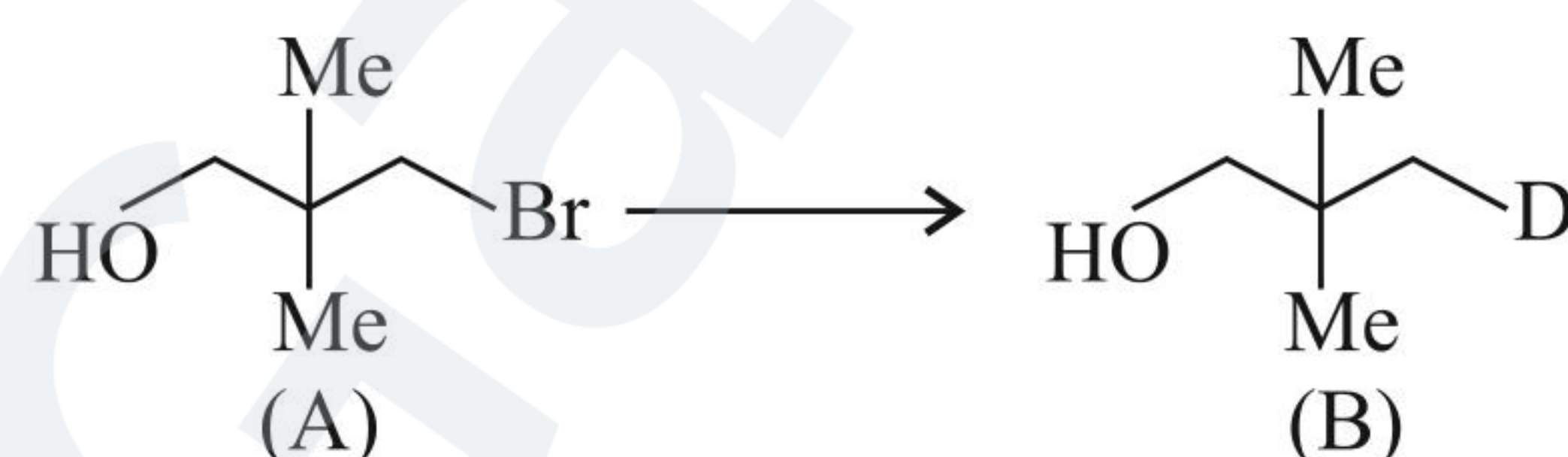
- (1) 1° alcohols (2) 2° alcohols
 (3) 3° alcohols (4) Hydroxy ketone

24. In the conversion of (A) to (B), the best method for the protection of (OH) group is:

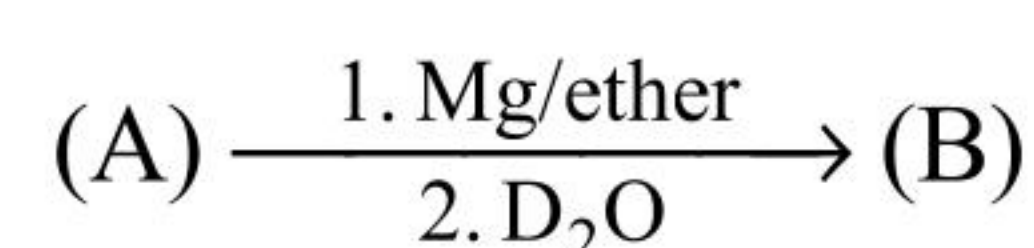


- (1) Benzylation method (2) Silylation method
 (3) ROTHP method (4) Both (1) and (2)

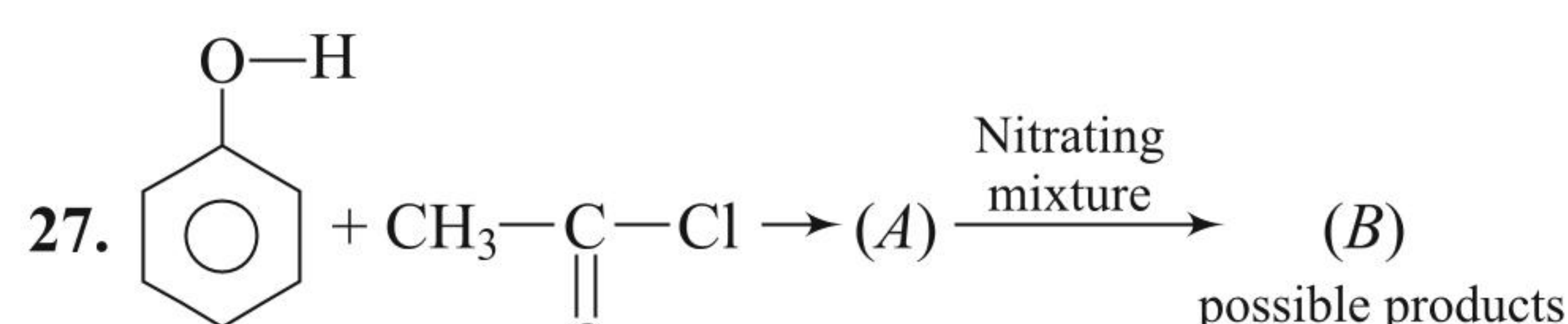
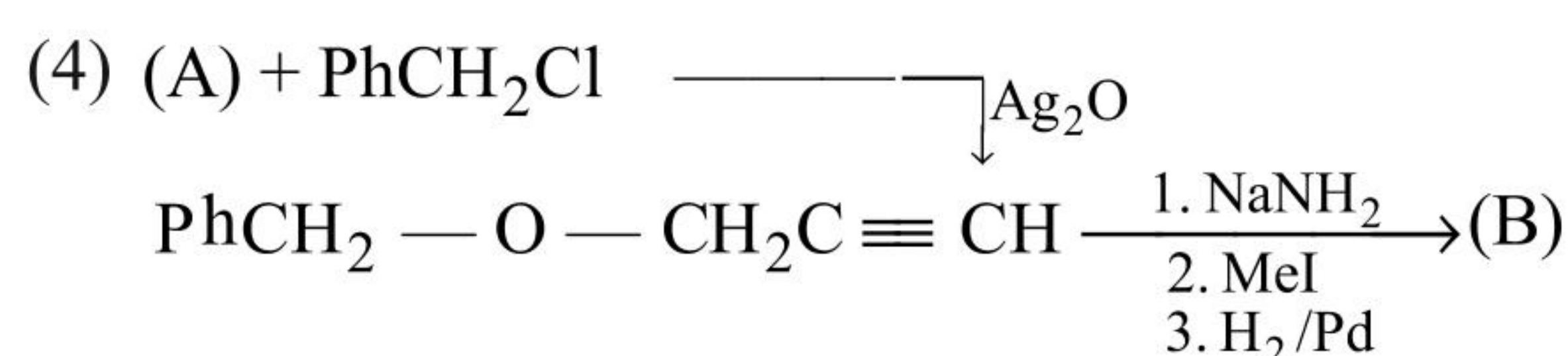
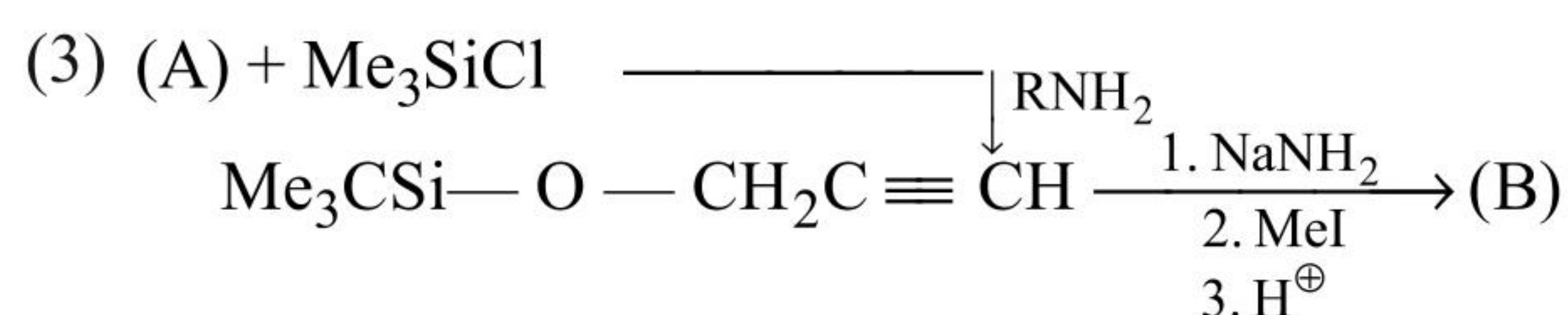
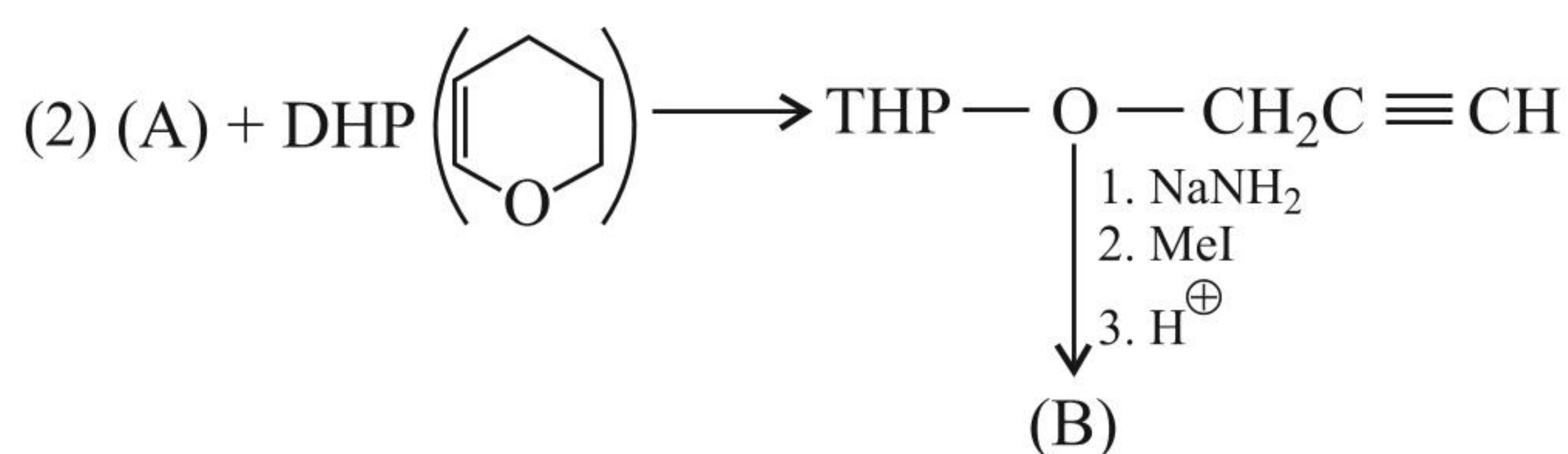
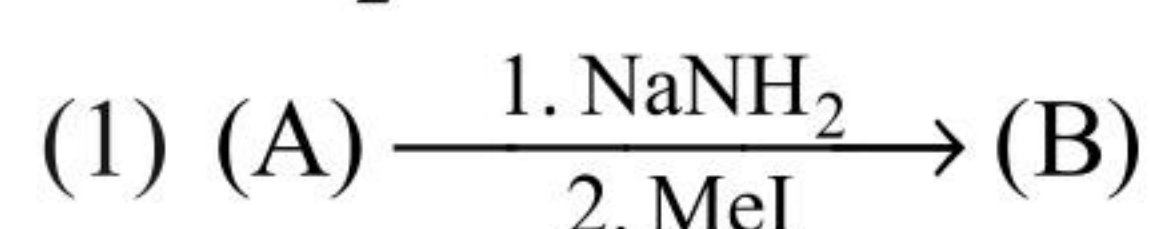
25. In the conversion of (A) to (B), the best method for the protection of (OH) group is silylation method because:



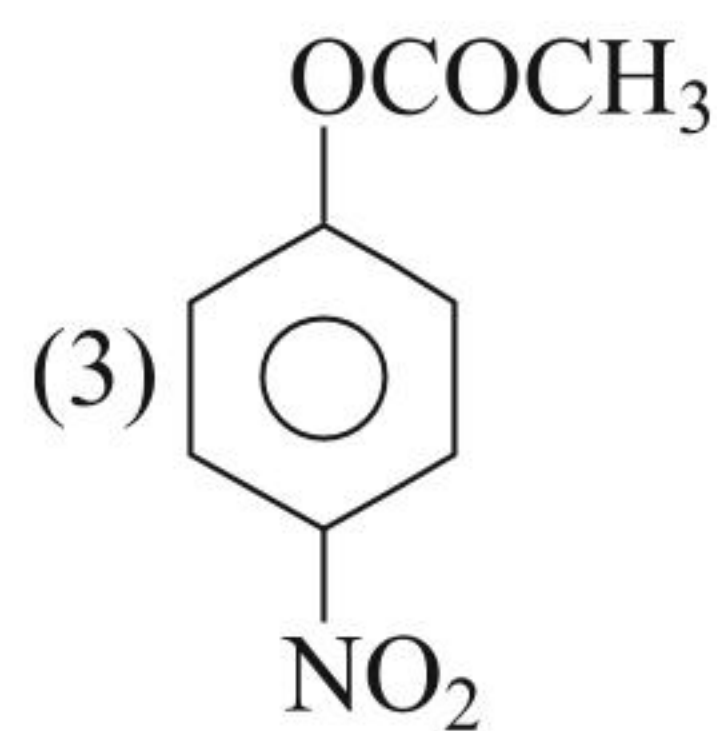
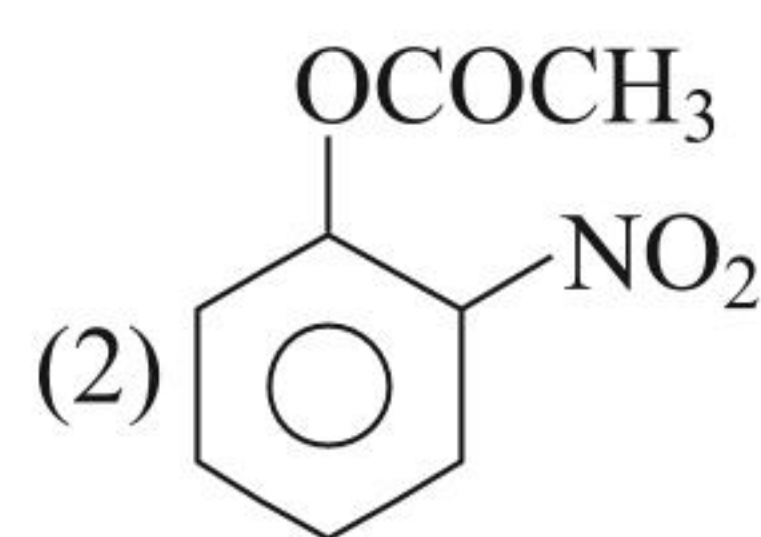
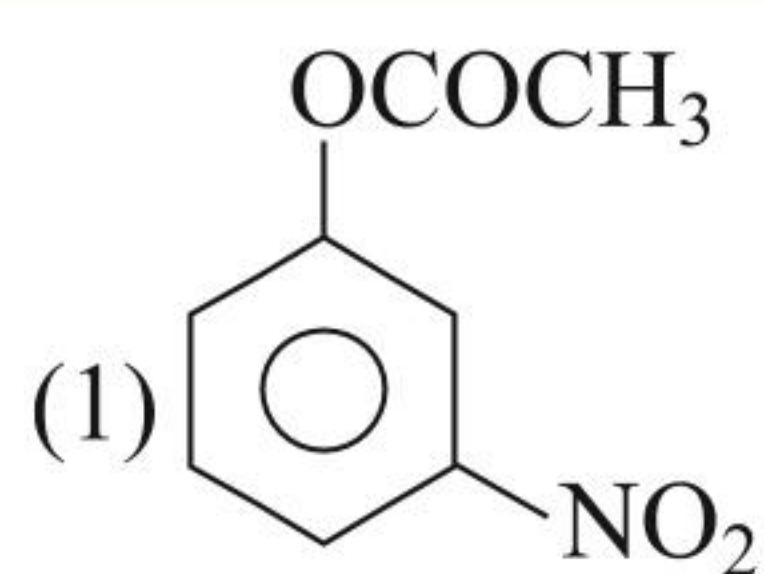
- (1) Benzylation method is not effective as Ag_2O might react with Br group of the reactant to give an (OH) group.
 (2) ROTHP cannot be used because the alcohol is likely to rearrange under the acidic conditions of ether formation.
 (3) Silylation method is effective since (OH) group is not sterically hindered.
 (4) The reaction can be carried out without protecting (OH) group, as shown below:



26. In the conversion of (A) $\text{HOCH}_2\text{C}\equiv\text{CH}$ to (B) $\text{HOCH}_2\text{C}\equiv\text{C—Me}$, the best method is:

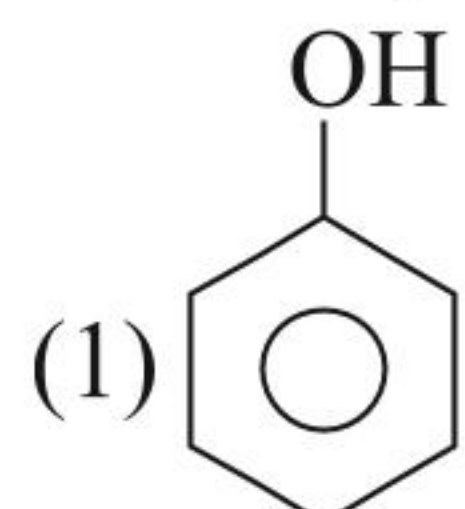


Possible structure of (B) is/are:

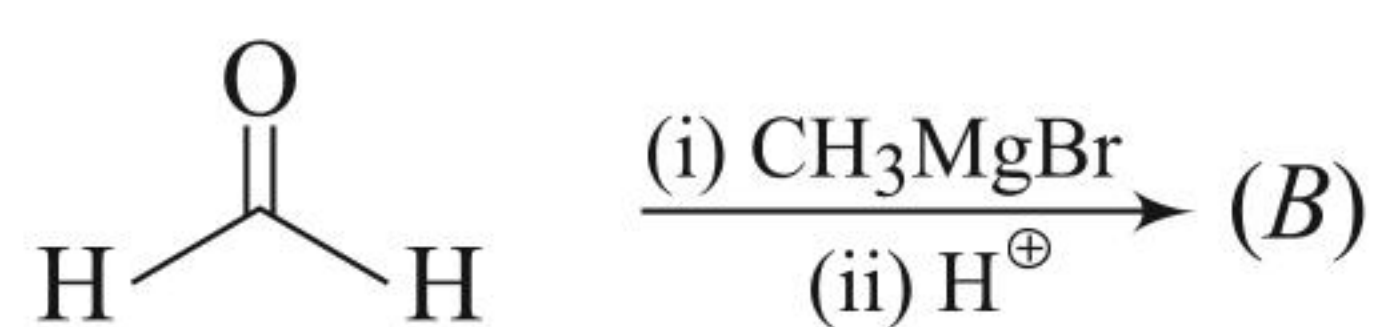
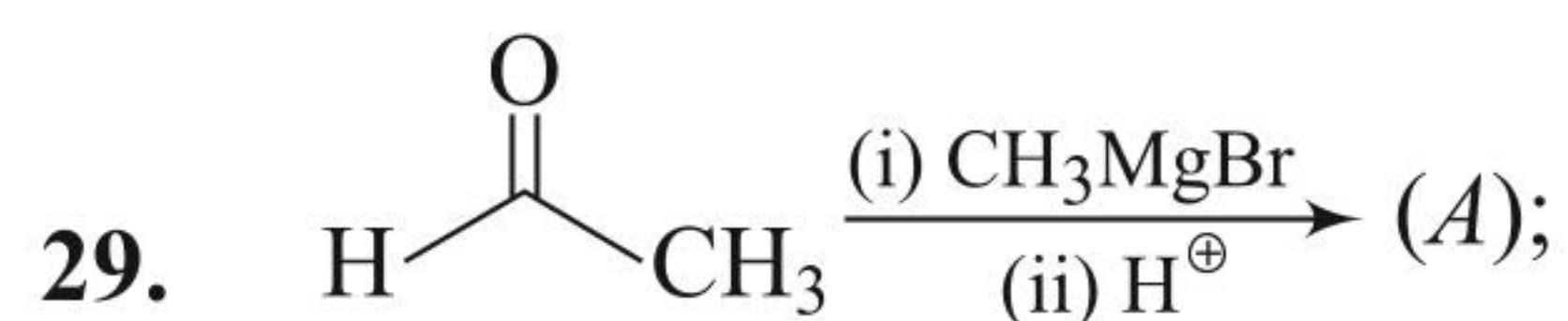
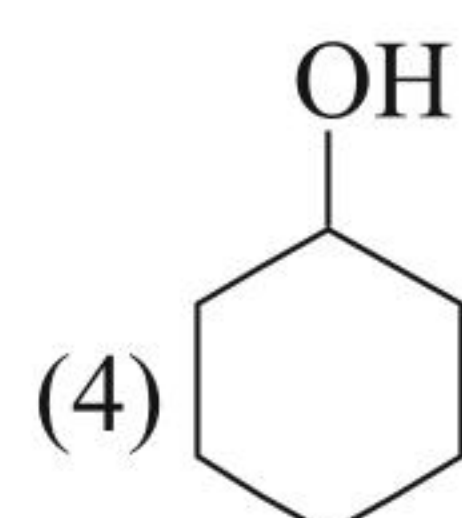
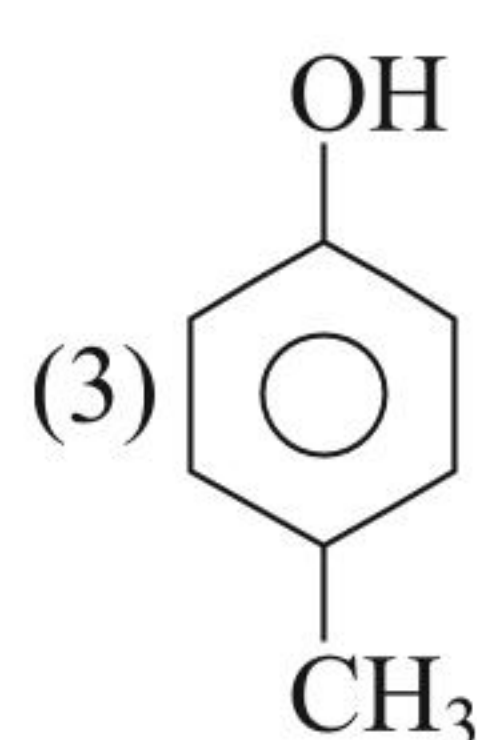


(4) All of these

28. Which of the following compounds do/does react with NaHCO_3 ?



(2) $\text{CH}_3\text{—C}\equiv\text{C—H}$



Which of the following reagents can be used to differentiate between *A* and *B*?

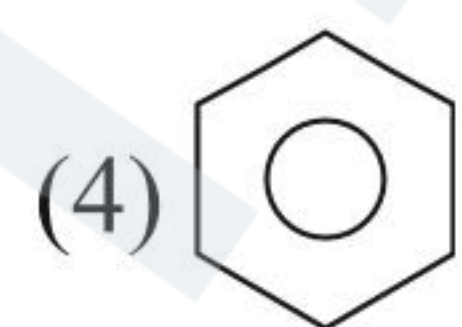
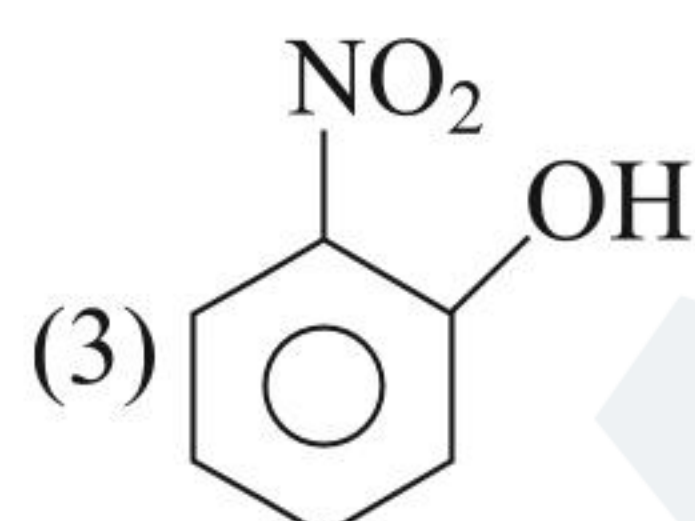
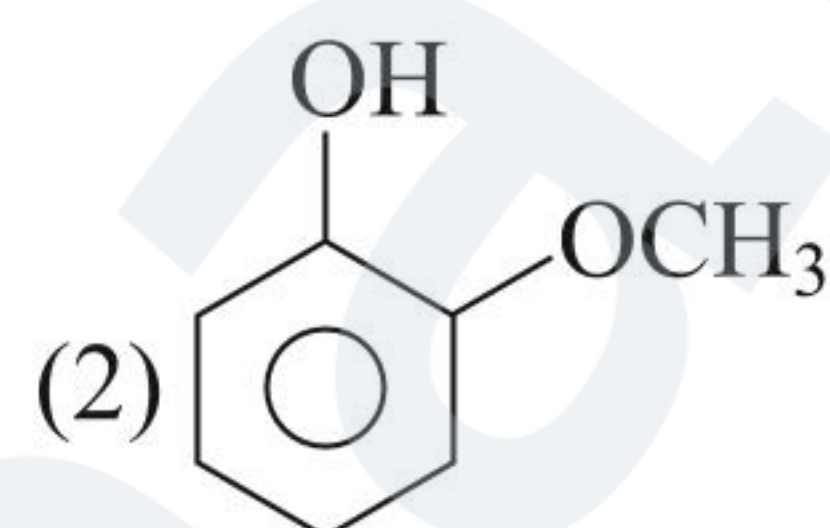
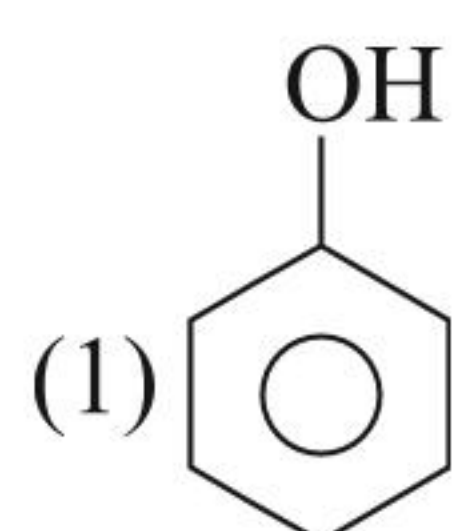
(1) Na

(2) FeCl_3

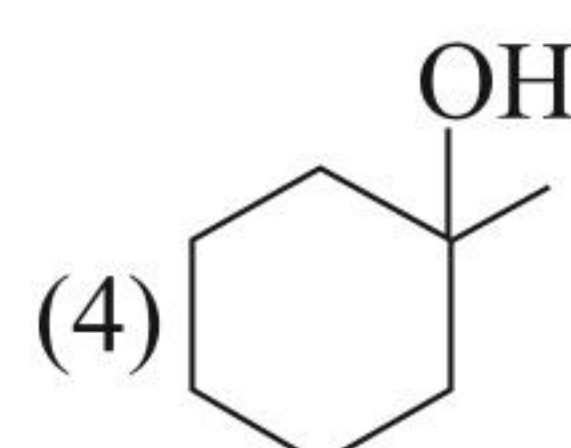
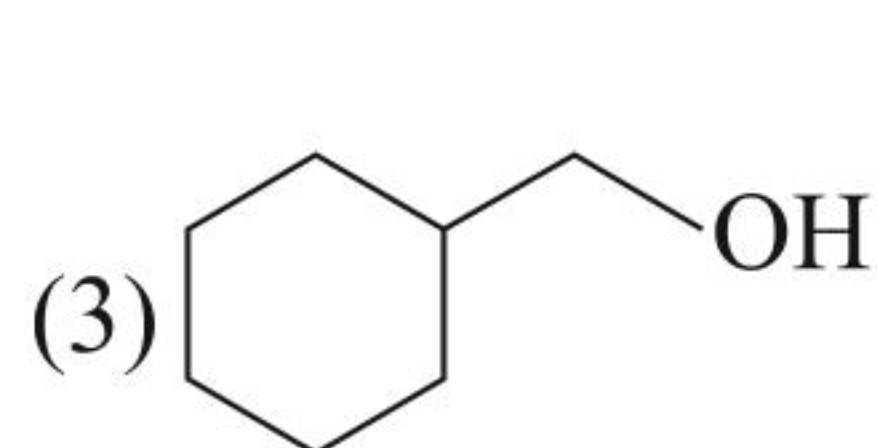
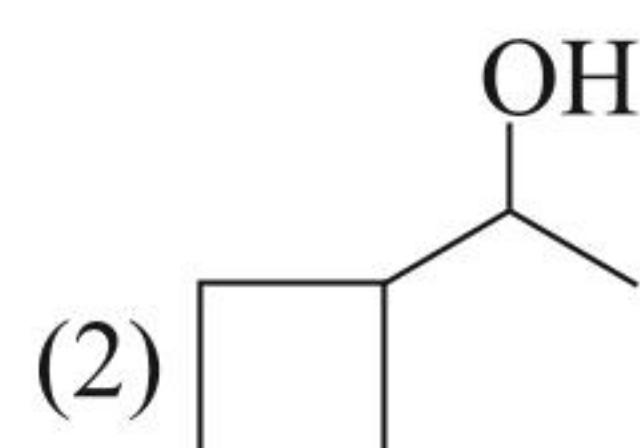
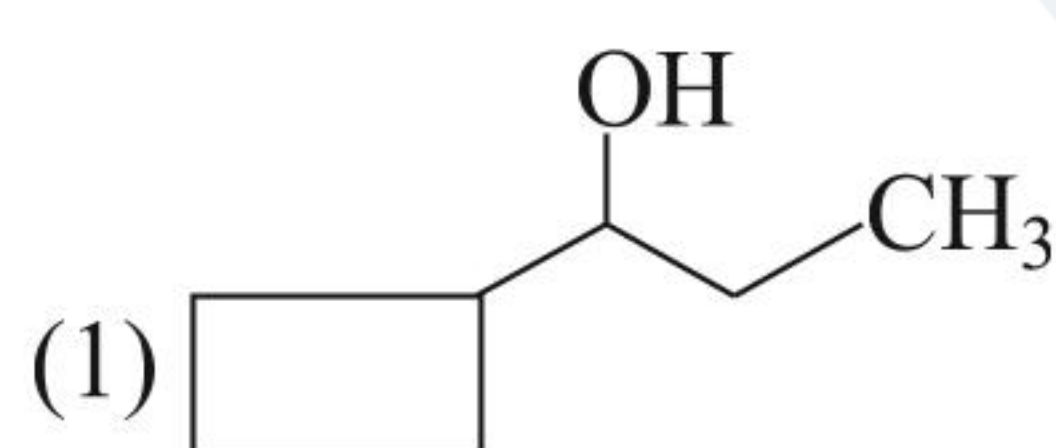
(3) Lucas reagents

(4) $\text{K}_2\text{Cr}_2\text{O}_7$

30. Which of the following compounds may undergo Reimer-Tiemann reaction?



31. Which of the reaction ring expansion take place when protic acid is added to it?

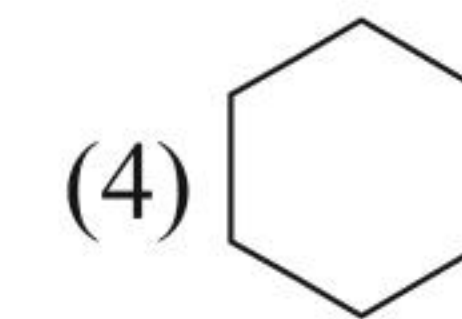


32. Which of the following compounds react with Na?

(1) Ph—OH

(2) CH_3OH

(3) $\text{CH}_3\text{—C}\equiv\text{CH}$

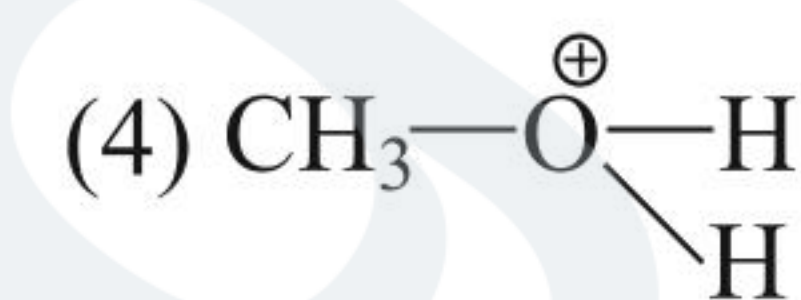


33. Which of the following is/are weaker acid than methanol?

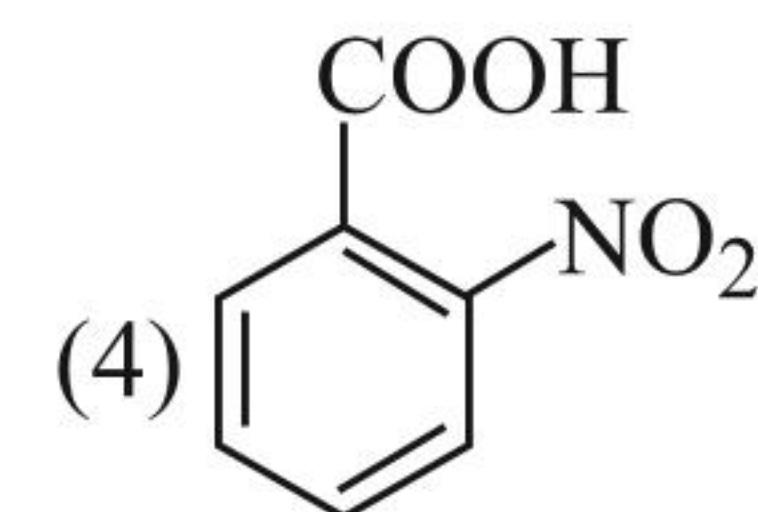
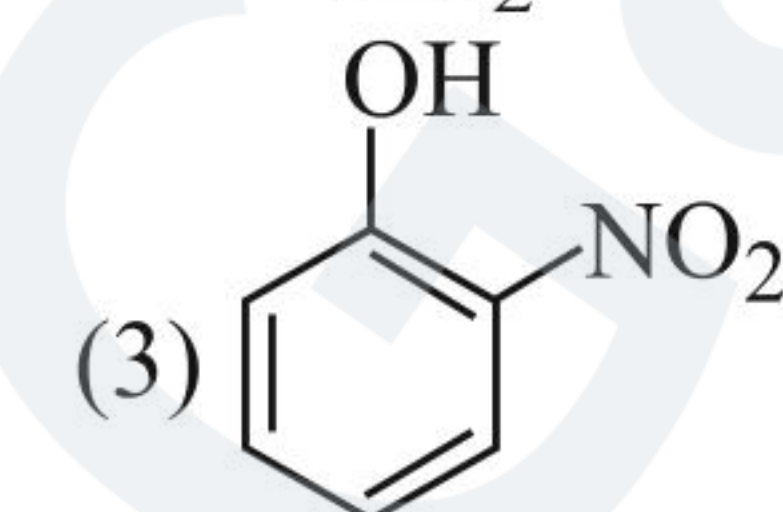
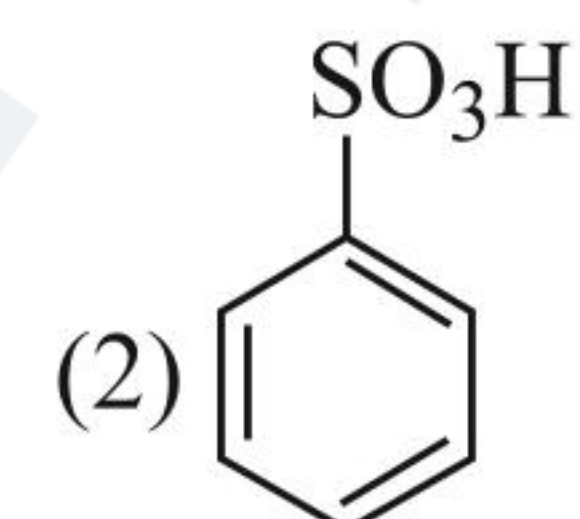
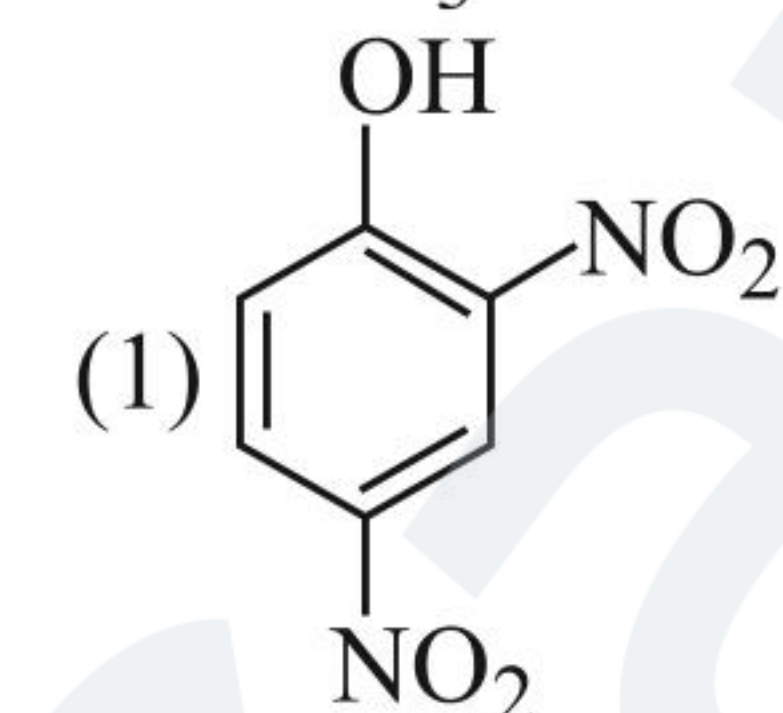
(1) $\text{CH}_3\text{—C}\equiv\text{CH}$



(3)



34. Which of the following compounds are soluble in NaHCO_3 ?



35. Isobutylene is obtained when

- (1) Sodium *t*-butoxide is treated with methyl iodide
- (2) *t*-Butyl bromide is treated with sodium methoxide
- (3) *t*-Butyl alcohol is treated with conc. H_2SO_4
- (4) *t*-Butyl methyl ether is heated with conc. H_2SO_4

36. In esterification reaction of alcohol ($\text{R}'\text{OH}$) with carboxylic (RCOOH) acid in presence of dry HCl gas is

- (1) $-\text{OH}$ of $\text{R}'\text{OH}$ is replaced by RCOO group of RCOOH
- (2) $-\text{OH}$ of RCOOH is replaced by $\text{R}'\text{O}$ of ROH

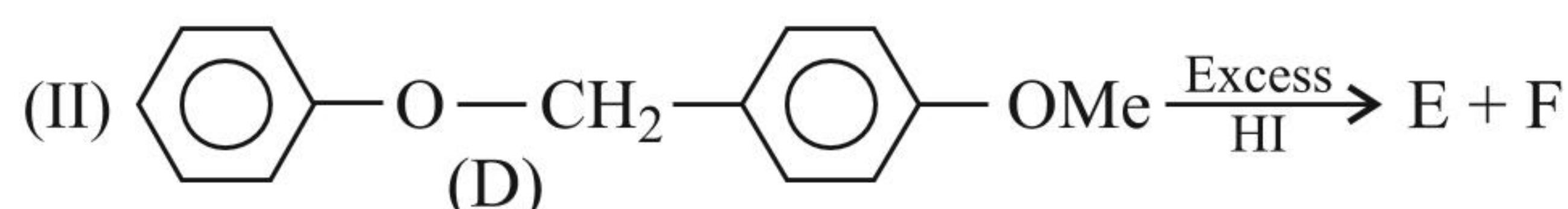
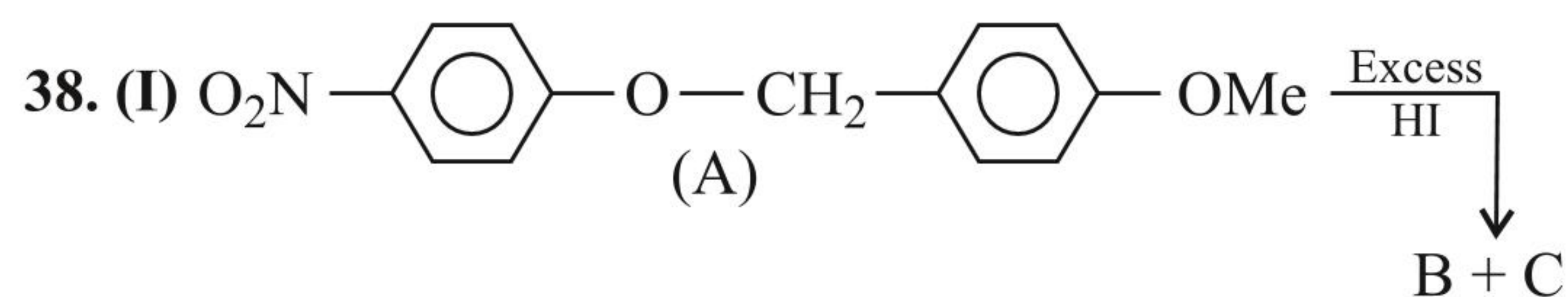
(3) $\text{R}'\text{OH}$ acts as a nucleophile and attacks on $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ of RCOOH

(4) Bigger the size of R lesser the rate of esterification

37. Phenol can be converted into salicylic acid by using:

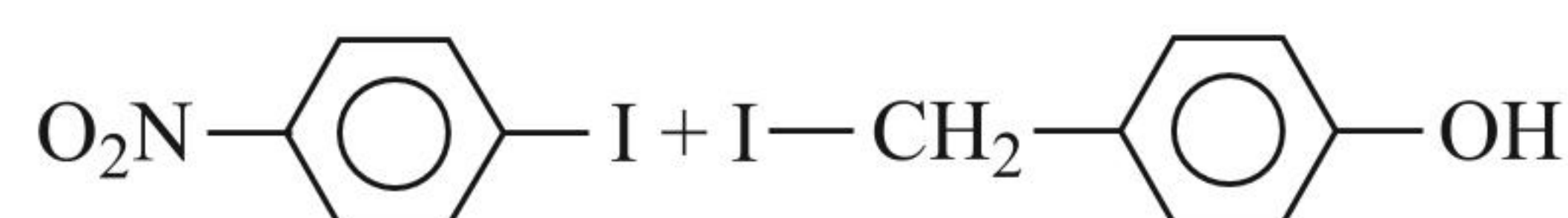
- (1) CO_2 and alkali under pressure followed by acidic hydrolysis.
- (2) CCl_4 and alkali at 340 K followed by acidic hydrolysis
- (3) CHCl_3 and alkali at 340 K followed by oxidation
- (4) None of these

Ethers

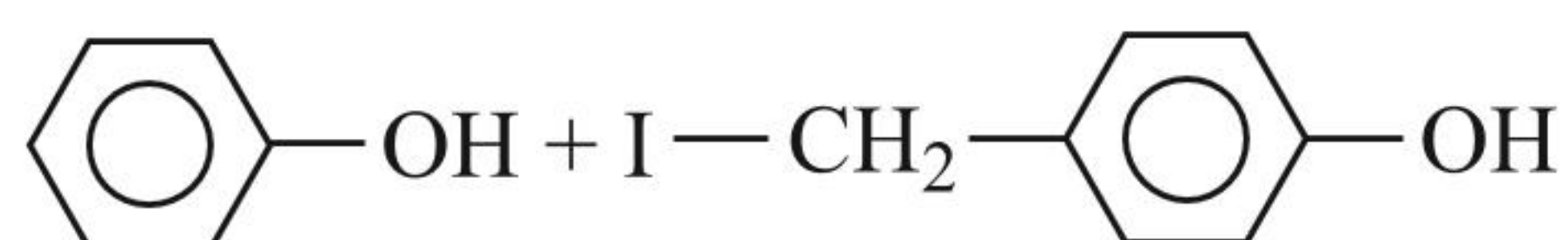


Which of the following statements is/are correct about the above reaction?

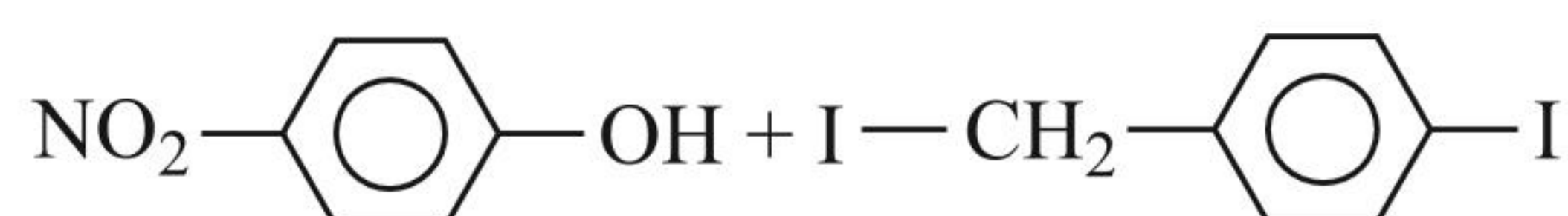
(1) The compounds (B) and (C), respectively, are:



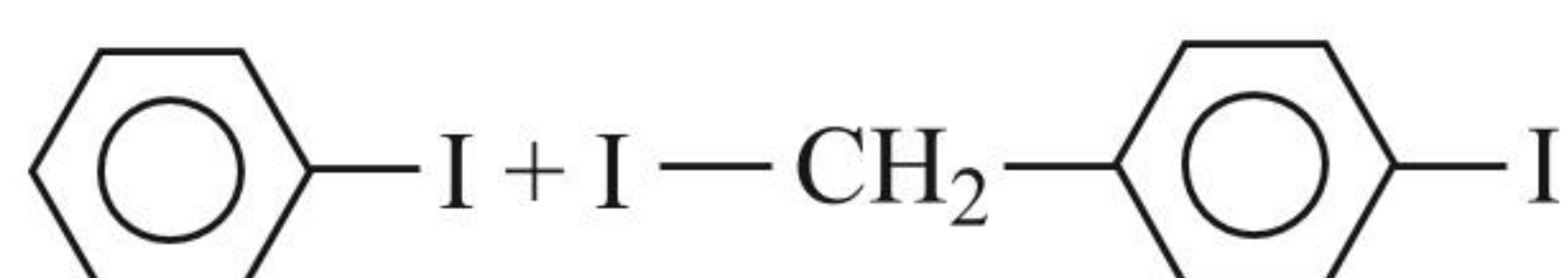
(2) The compounds (E) and (F), respectively, are:



(3) The compounds (B) and (C), respectively, are:

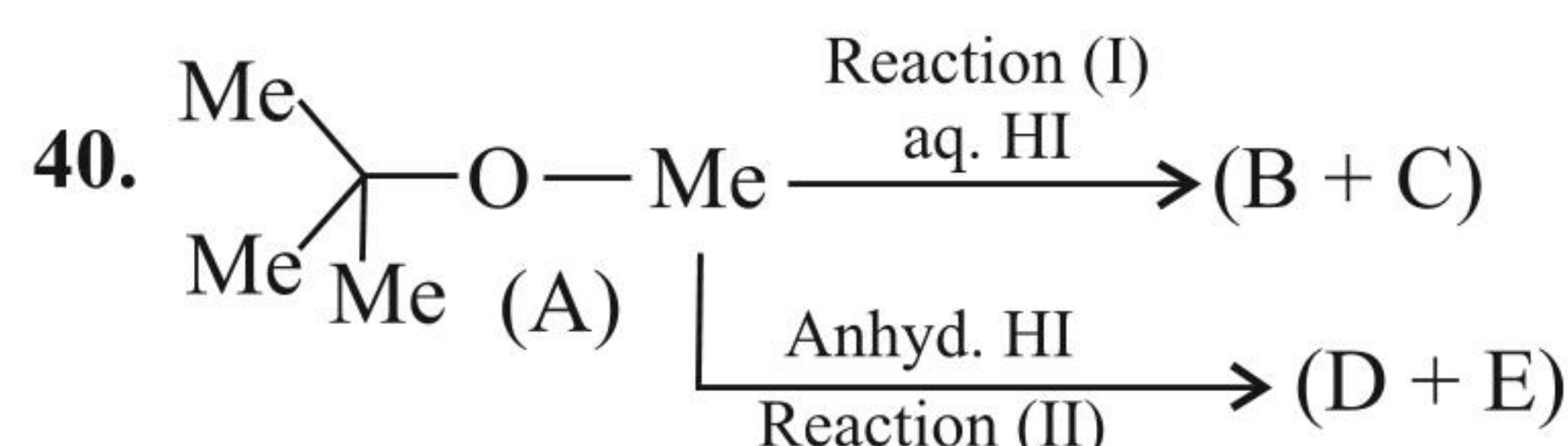


(4) The compounds (E) and (F), respectively, are:



39. In Q. No. 38, which of the following statements is/are correct?

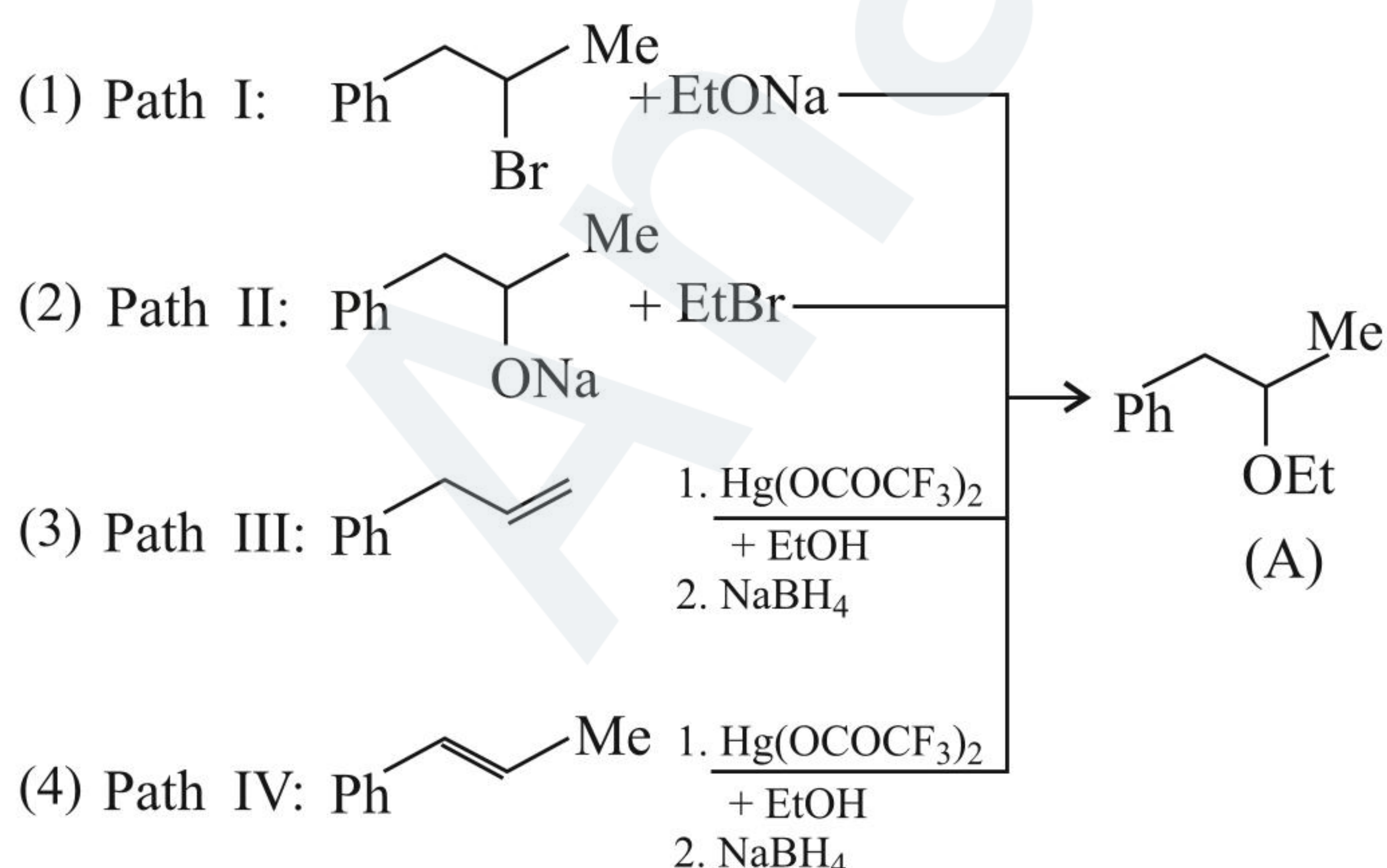
- (1) Both reactions proceed by SN^1 mechanism.
- (2) Both reactions proceed by SN^2 mechanism.
- (3) Reaction (I) proceeds by SN^1 and reaction (II) by SN^2 mechanism.
- (4) Reaction (I) proceeds by SN^2 and reaction (II) by SN^1 mechanism.



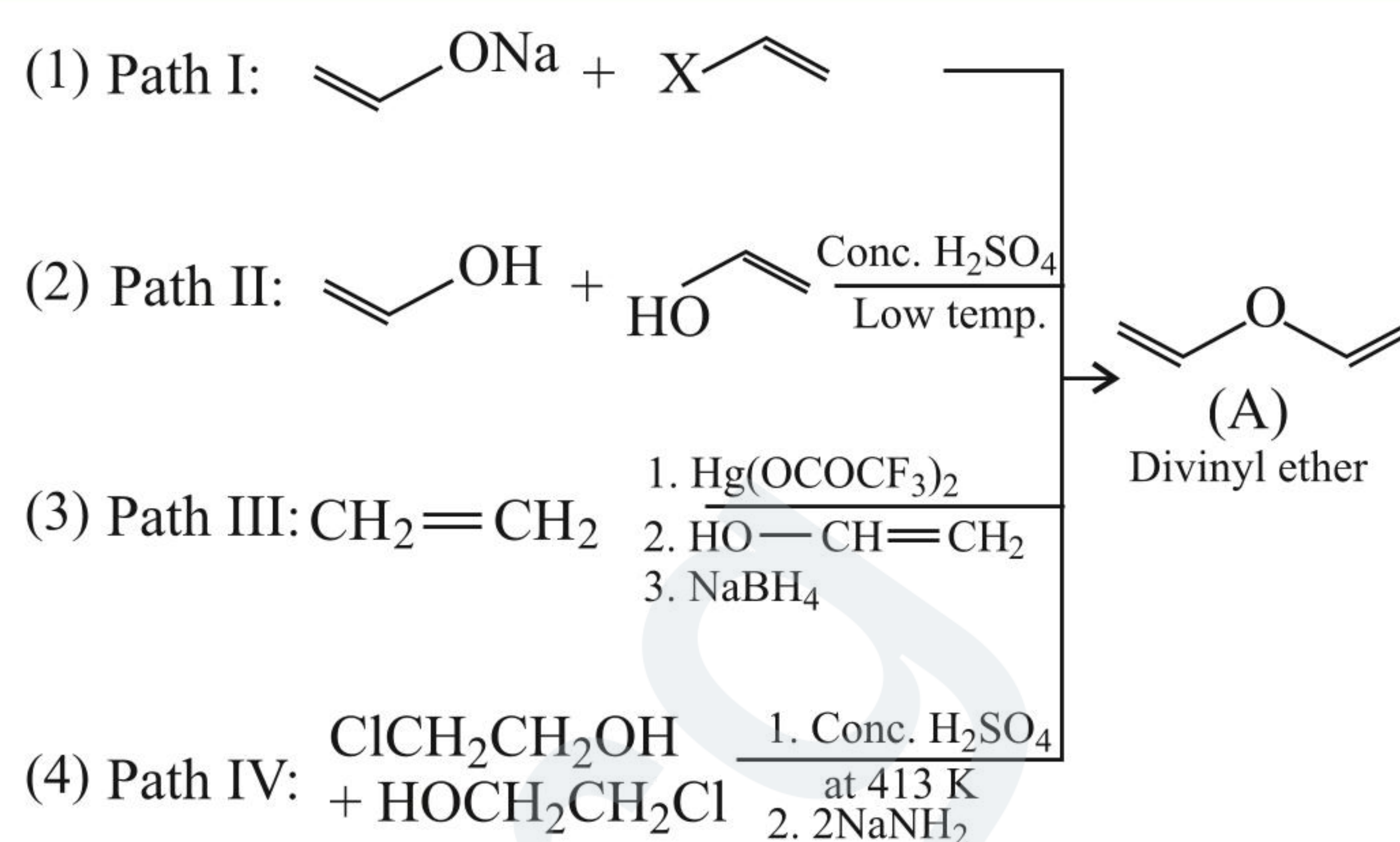
Which of the following statements is/are correct?

- (1) The compounds (B) and (C), respectively, are $\text{Me}_3\text{C}-\text{I} + \text{MeOH}$ and reaction (I) proceeds by SN^1 mechanism.
- (2) The compounds (B) and (C) respectively, are $\text{Me}_3\text{C}-\text{OH} + \text{MeI}$ and reaction (I) proceeds by SN^2 mechanism.
- (3) The compounds (E) and (F), respectively, are $\text{Me}_3\text{C}-\text{I} + \text{MeOH}$ and reaction (II) proceeds by SN^1 mechanism.
- (4) The compounds (E) and (F), respectively, are $\text{Me}_3\text{C}-\text{OH} + \text{MeOH}$ and reaction (II) proceeds by SN^2 mechanism.

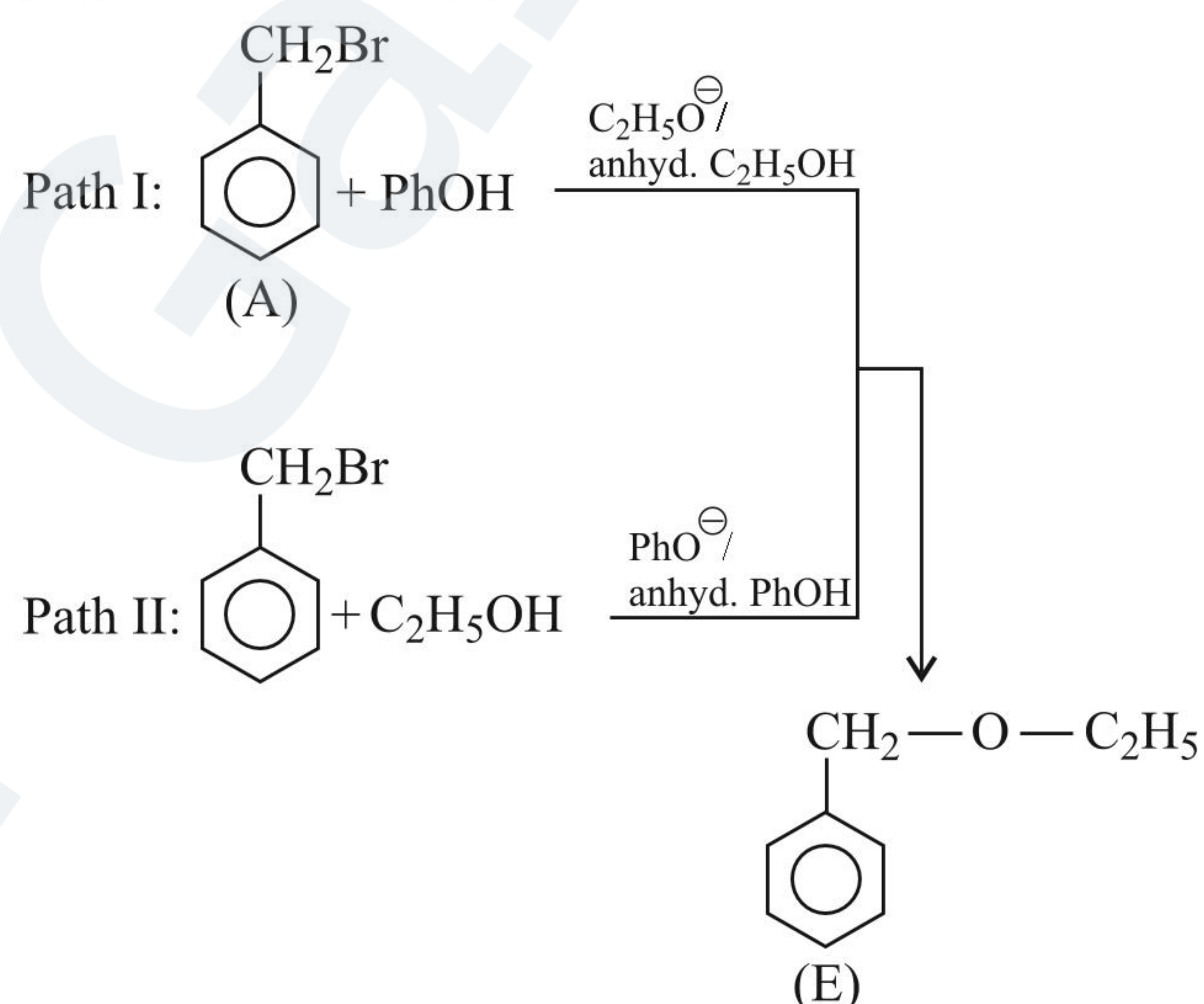
41. Which of the following paths is/are feasible for the preparation of ether (A)?



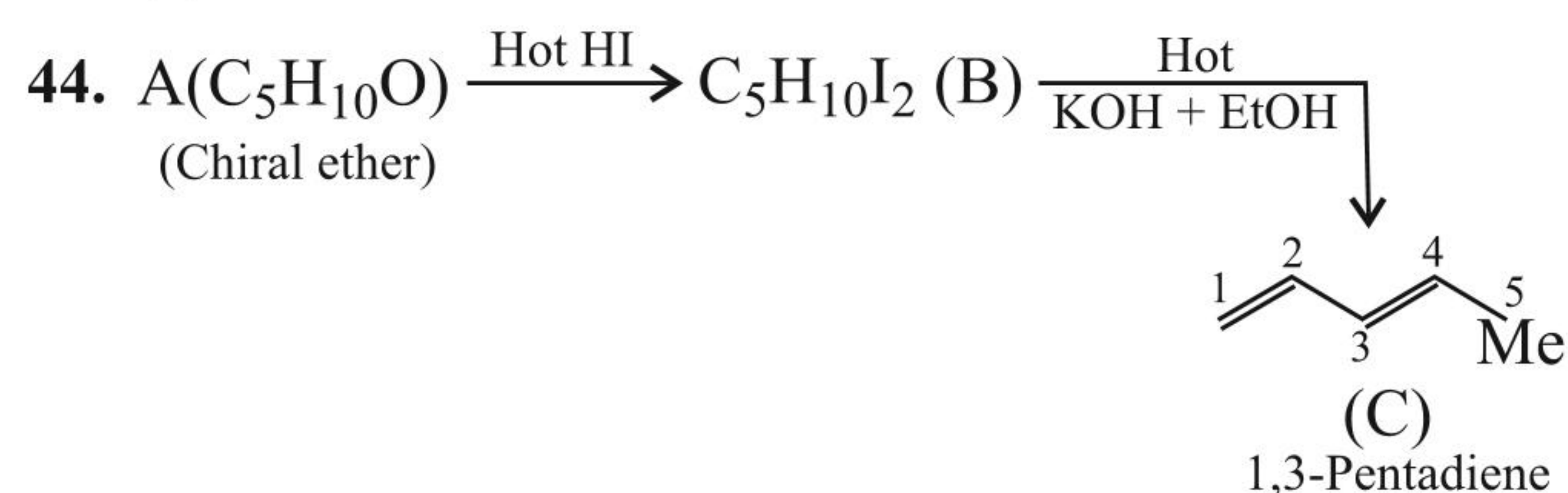
42. Which of the following paths is/are feasible for the preparation of ether (A)?



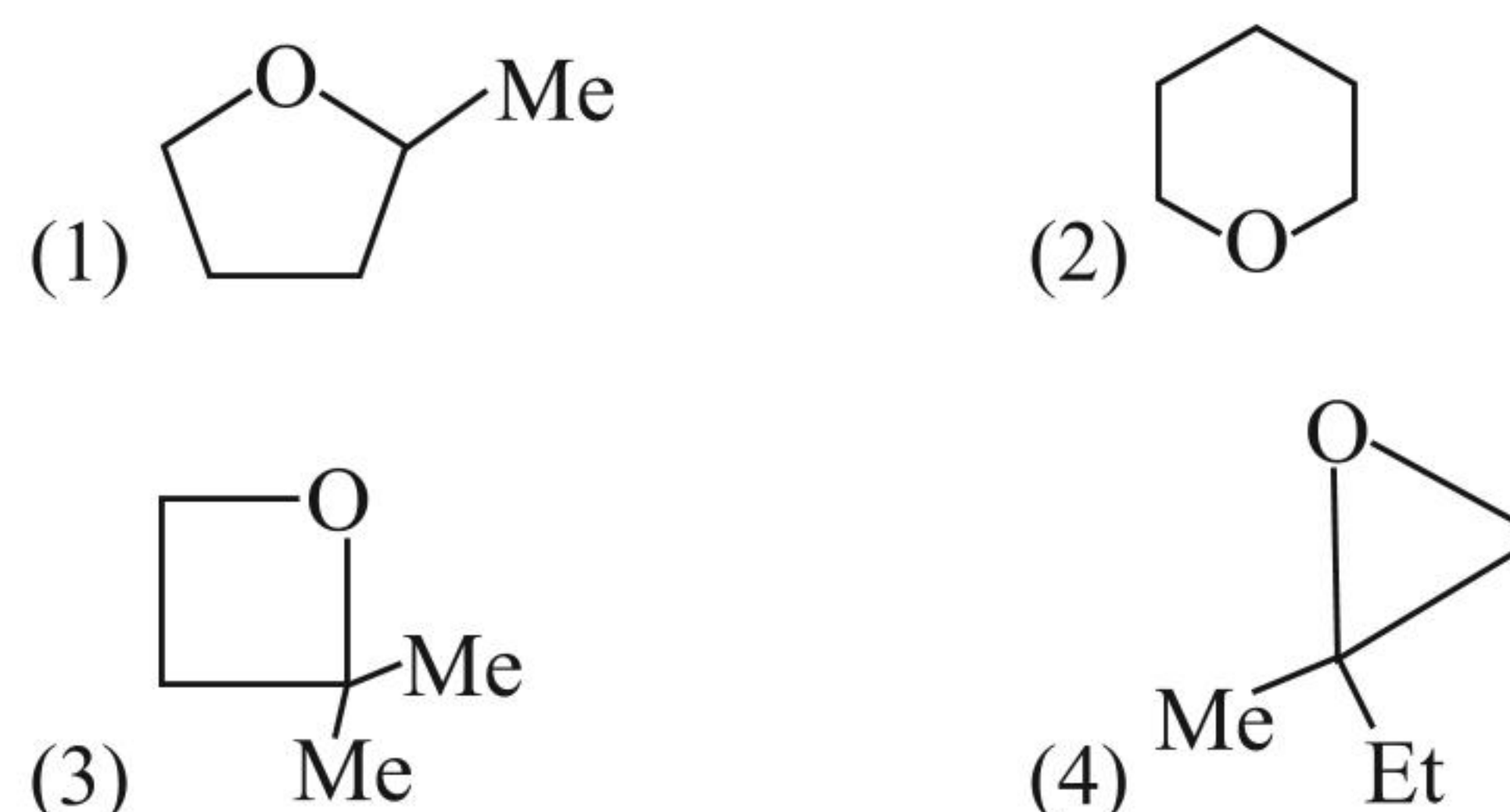
43. Which of the following paths is/are feasible for the preparation of ether (E)?



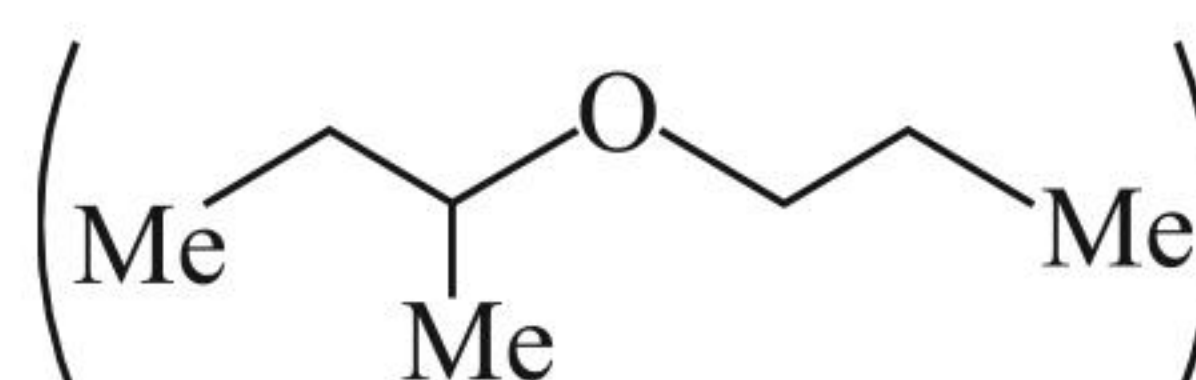
- (1) Path I is feasible.
- (2) Path II is feasible.
- (3) Both paths are feasible.
- (4) None is feasible.



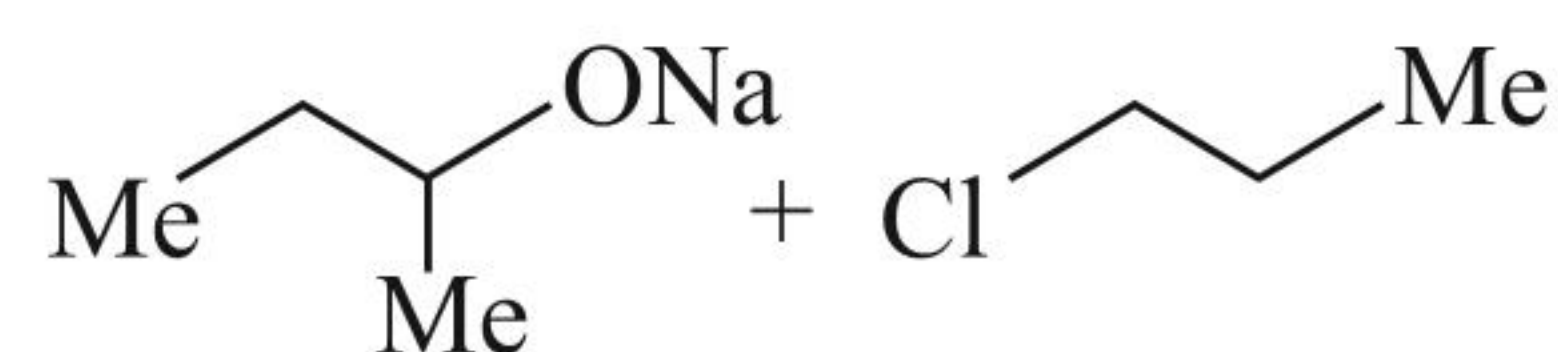
The structure of (A) is:



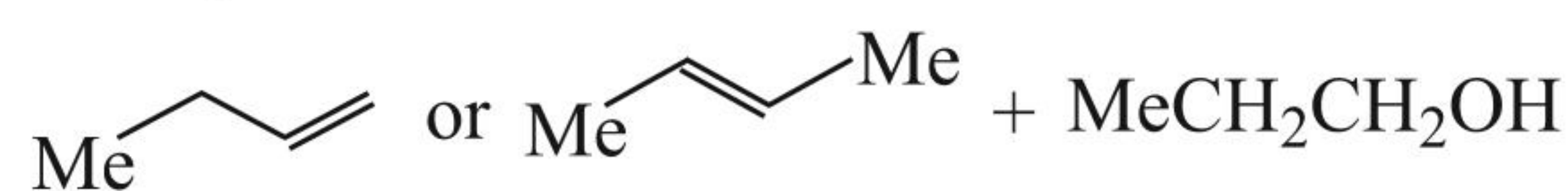
45. Which of the following reactions is feasible for the preparation of propyl *sec*-butyl ether (I)?



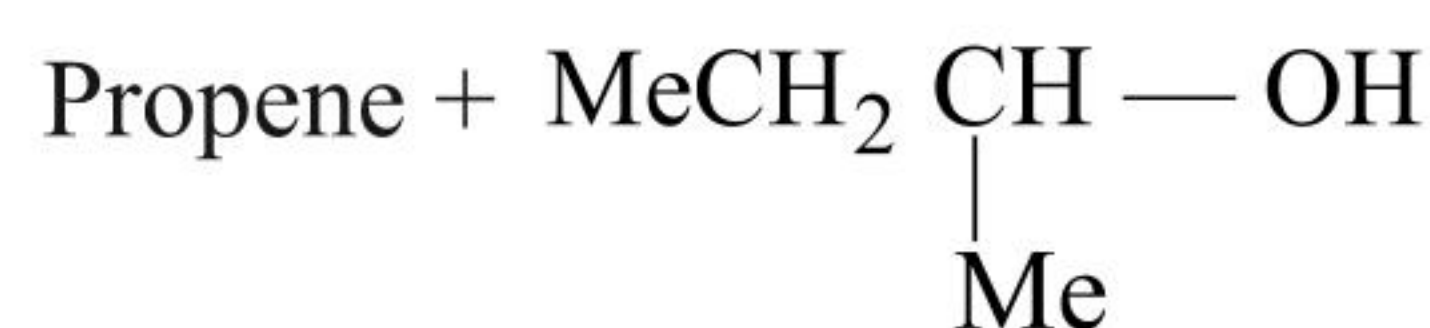
(1) Williamson's synthesis with



(2) Alkoxy mercuriation-demercuration of



(3) Alkoxy mercuriation-demercuration of

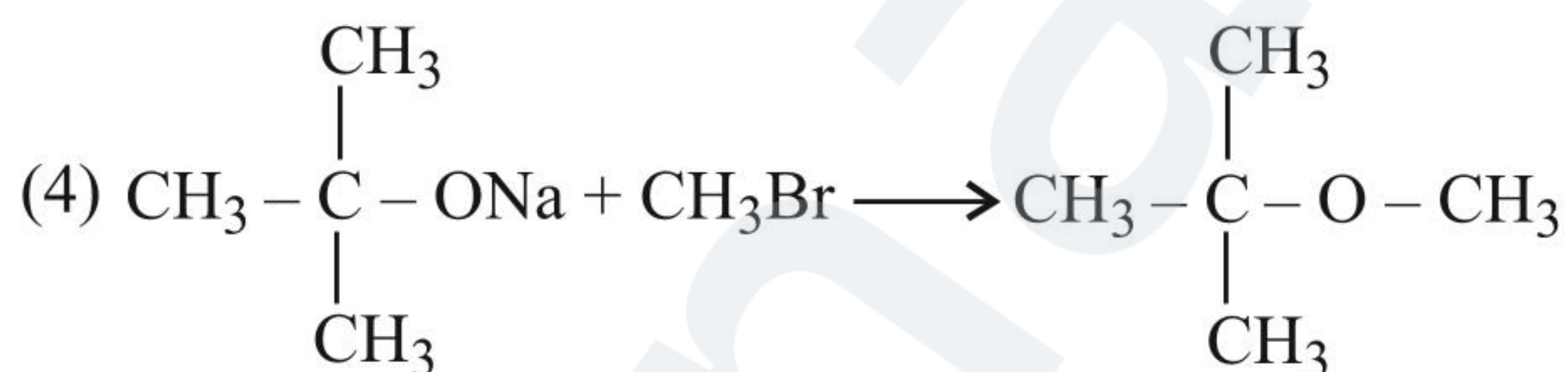
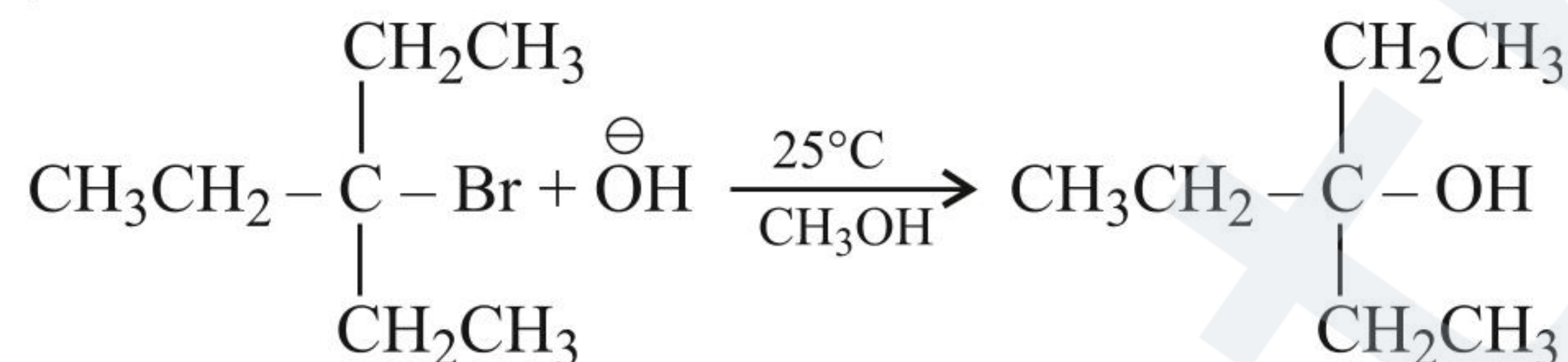
(4) Intermolecular dehydration of $\text{MeCH}_2\text{CH}(\text{Me})\text{OH}$ and $\text{MeCH}_2\text{CH}_2\text{OH}$.

46. Which of the following reactions is feasible for the preparation of 1-propoxy-2-methyl propane (I)?

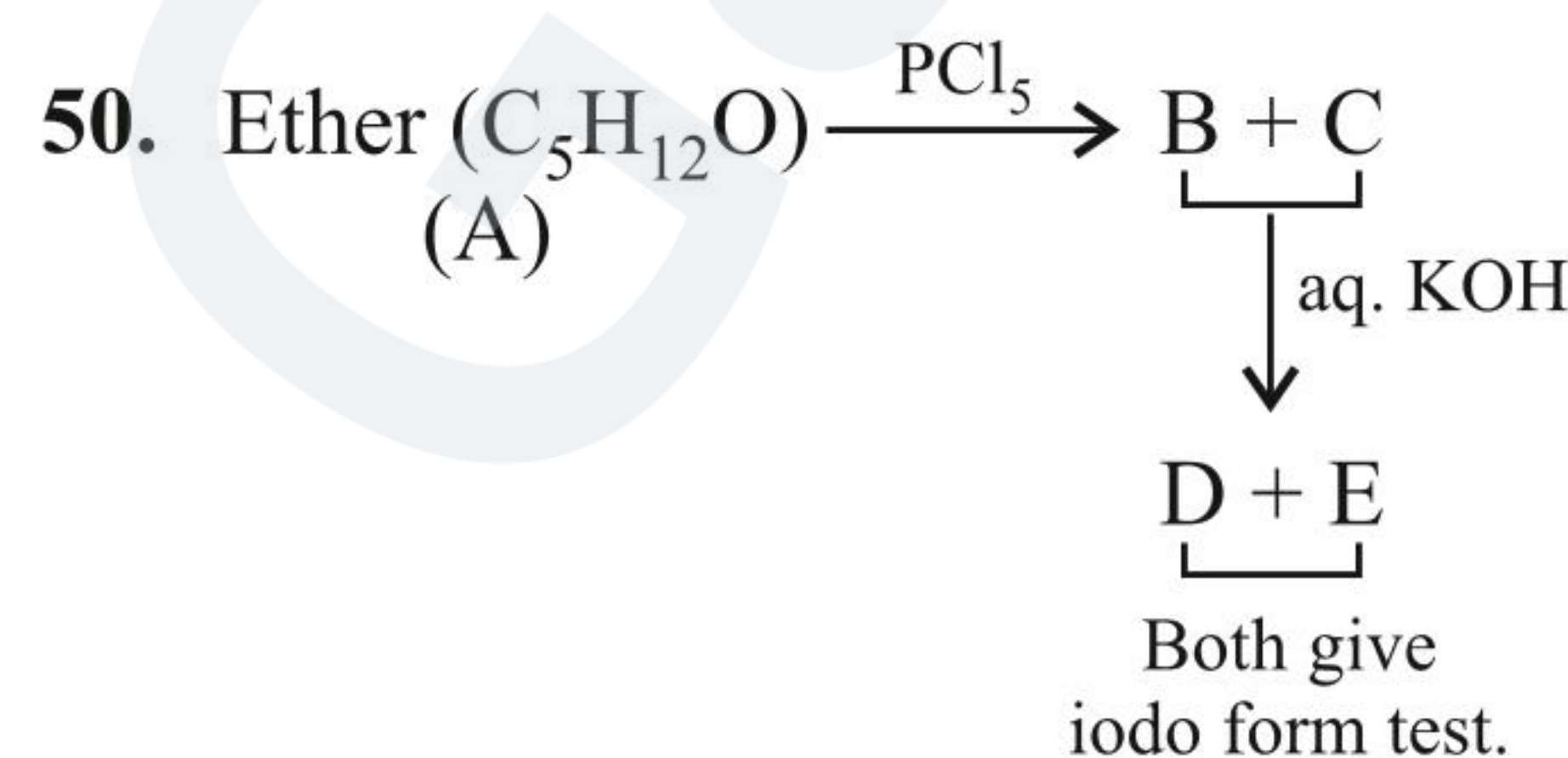
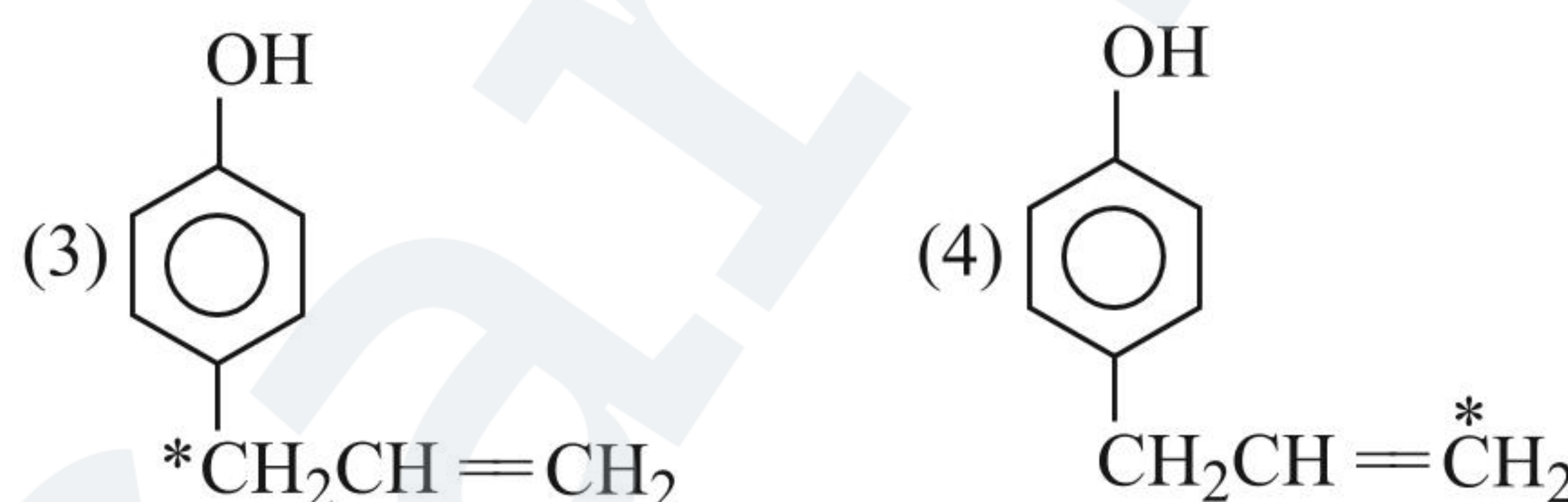
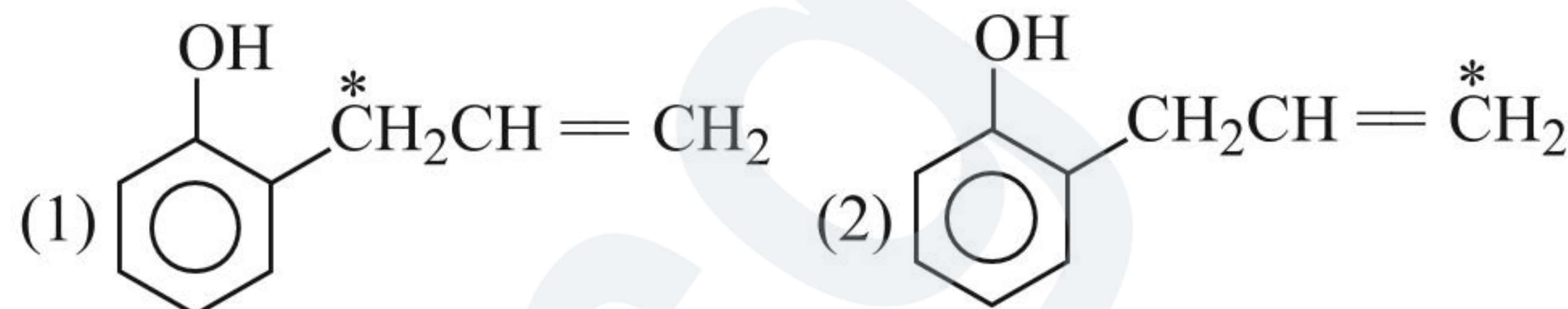
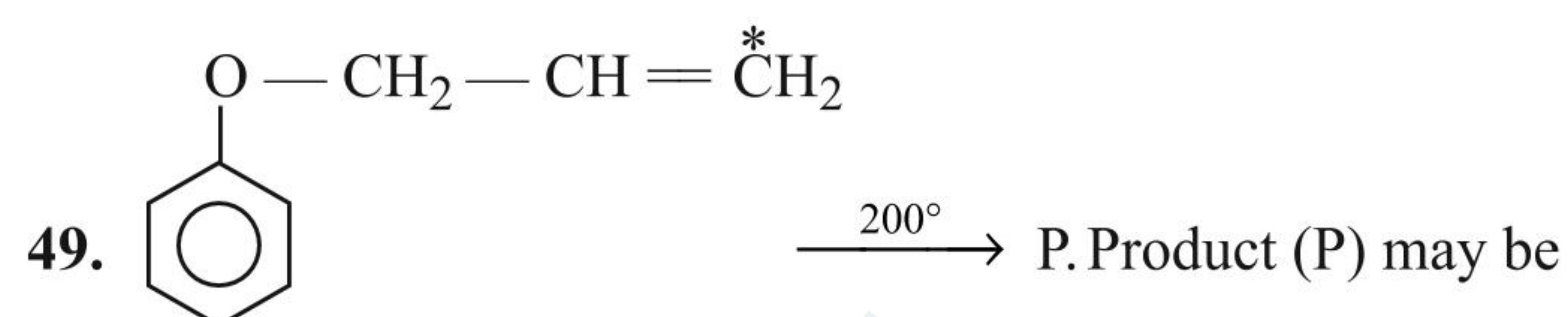
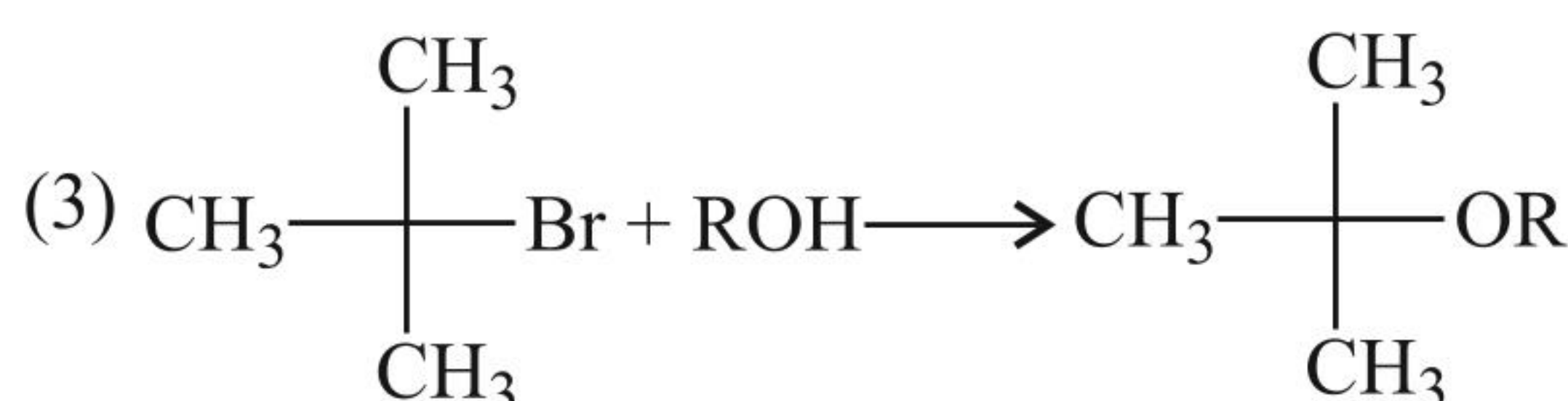
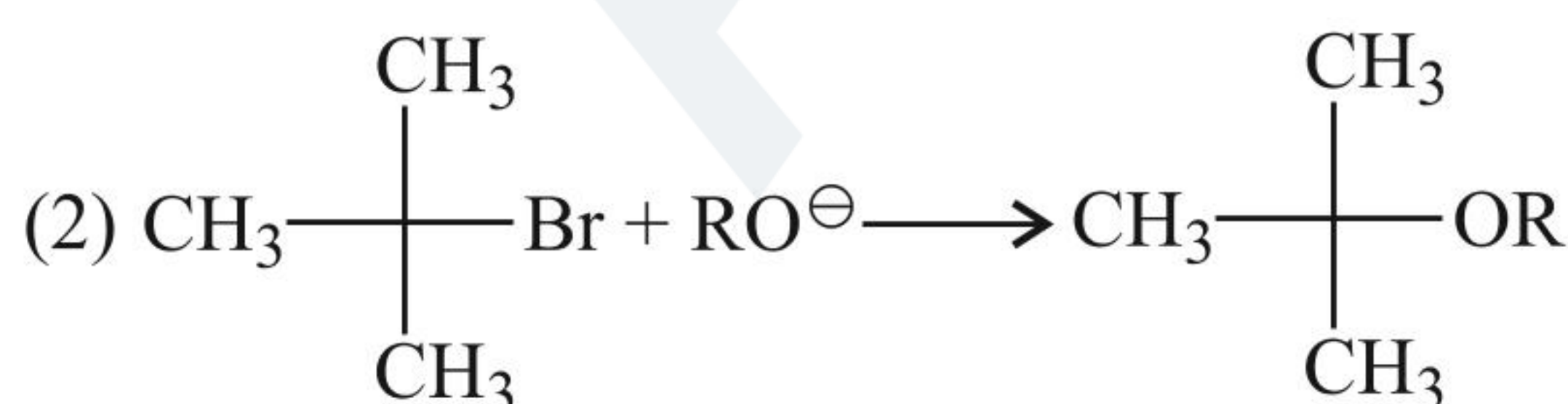
(1) Williamson's synthesis of $(\text{Me}_2\text{CHCH}_2\text{ONa} + \text{MeCH}_2\text{CH}_2\text{Cl})$.(2) Williamson's synthesis of $(\text{Me}_2\text{CHCH}_2\text{Cl} + \text{MeCH}_2\text{CH}_2\text{ONa})$.(3) Alkoxy mercuriation-demercuration of $(\text{Me}_2\text{CH}=\text{CH}_2 + \text{MeCH}_2\text{CH}_2\text{OH})$.(4) Alkoxy mercuriation demercuration of propene with $\text{Me}_2\text{CHCH}_2\text{OH}$.

47. Which of the following reaction are feasible?

(1)



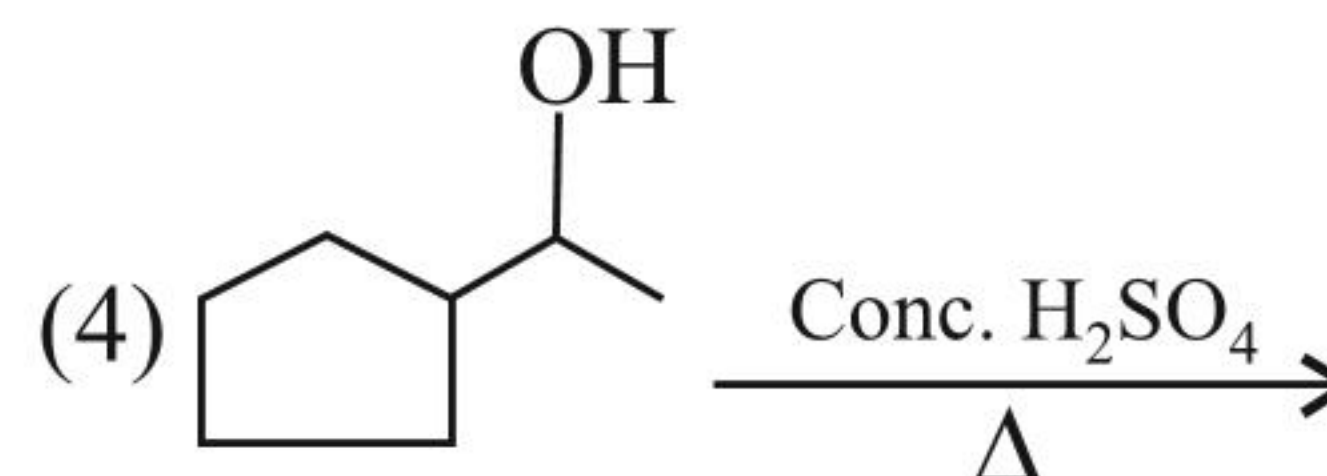
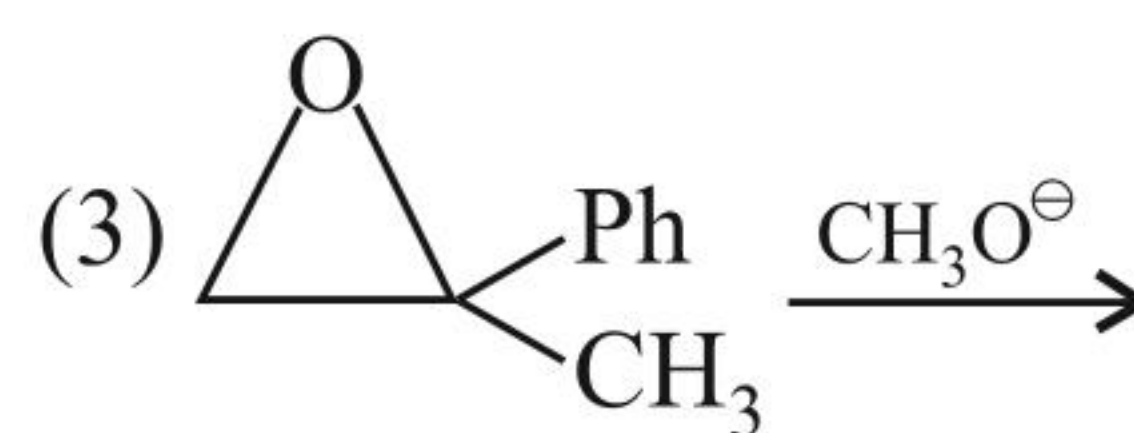
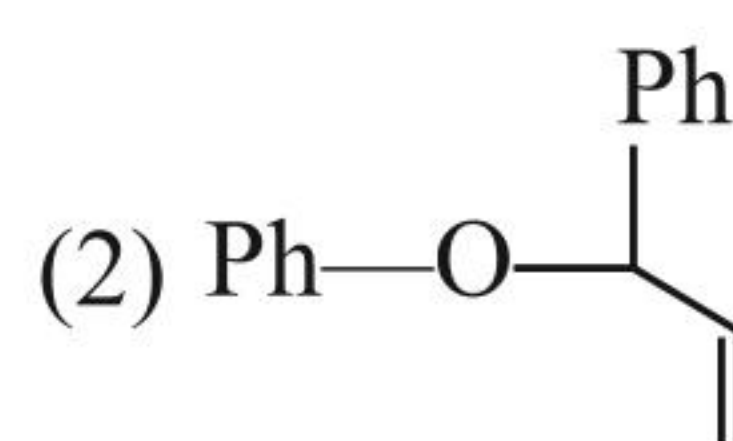
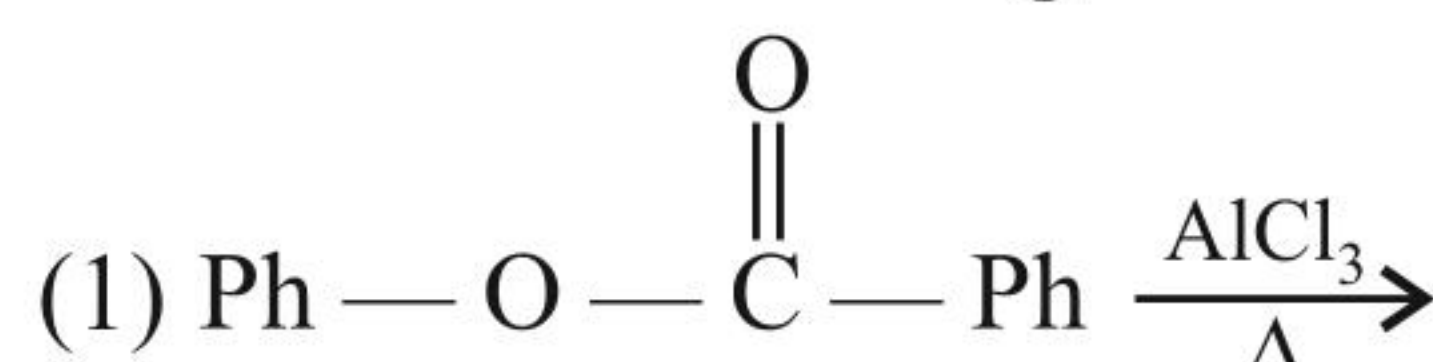
48. Which of the following reaction are not feasible?



Select the correct answer:

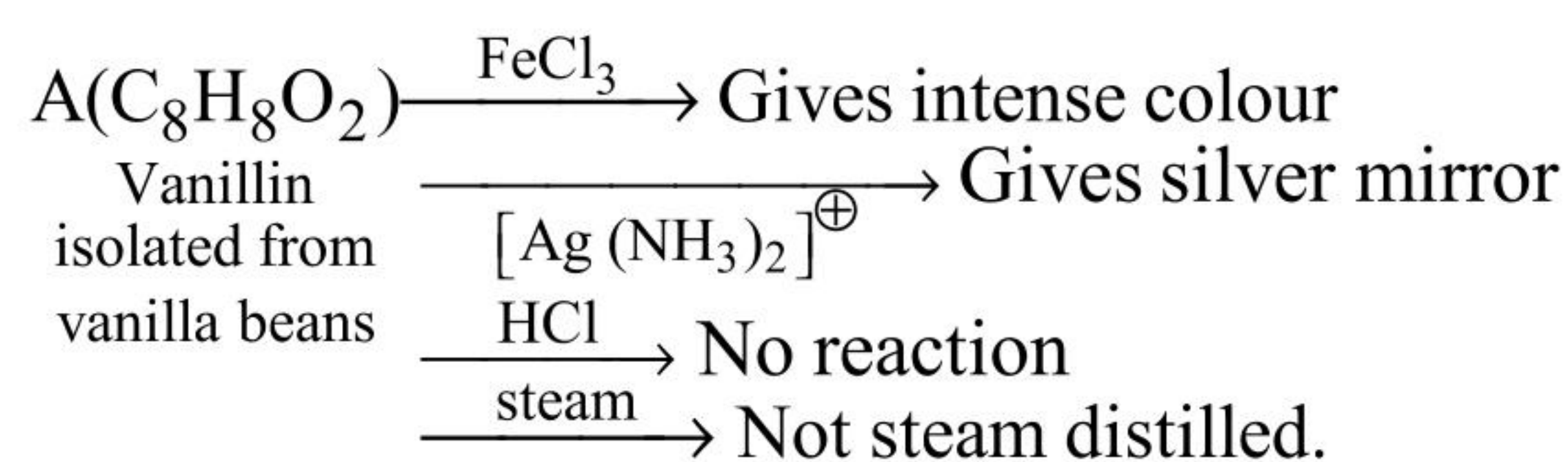
(1) A is: $\text{C}_2\text{H}_5-\text{O}-\text{CH}_2\text{CH}_3$ (2) C is: $\text{C}_3\text{H}_7\text{Cl}$.(3) C is: $(\text{CH}_3)_2\text{CHCl}$.(4) E is: $(\text{CH}_3)_2\text{CHOH}$

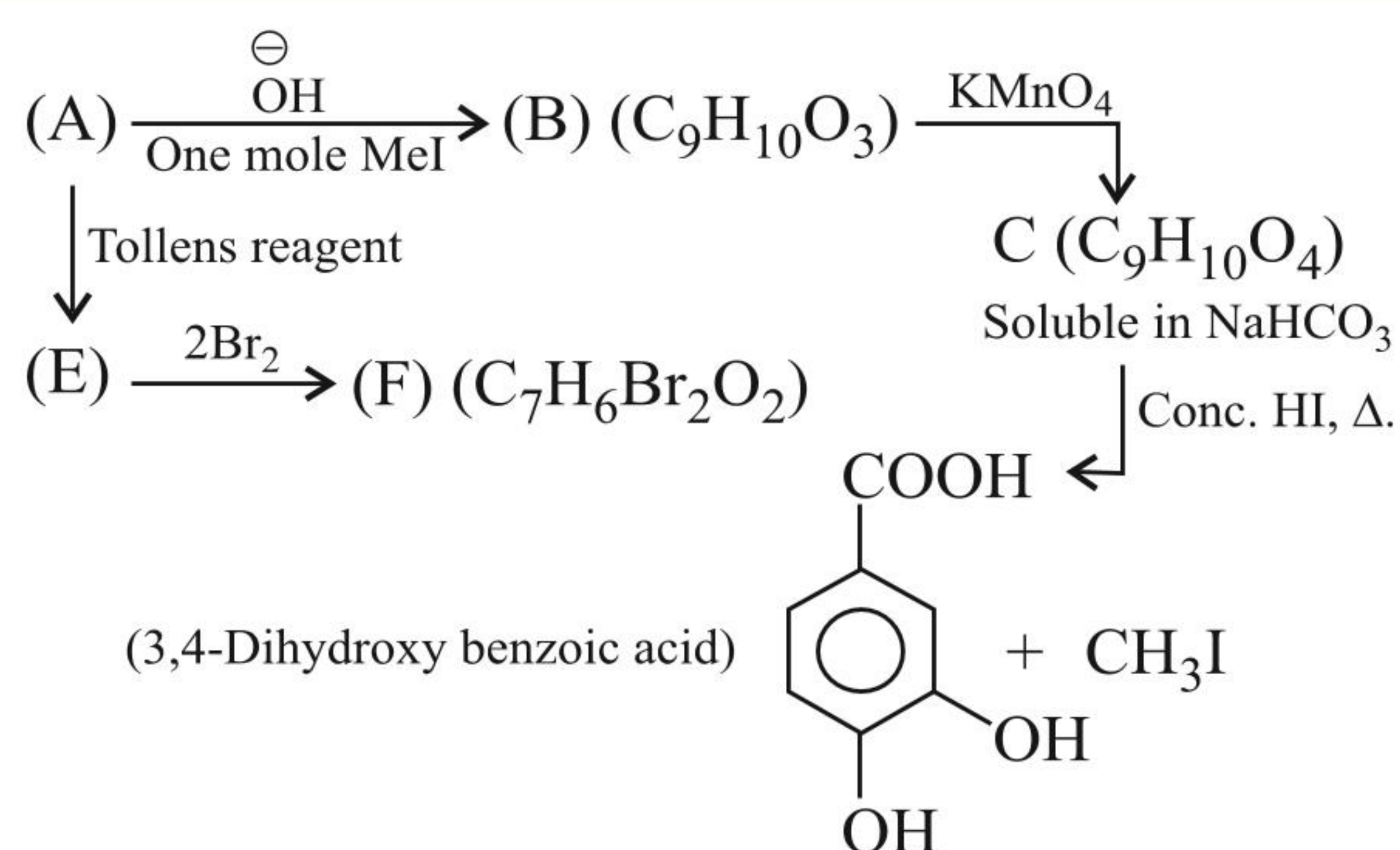
51. Which of the following involve rearrangement?



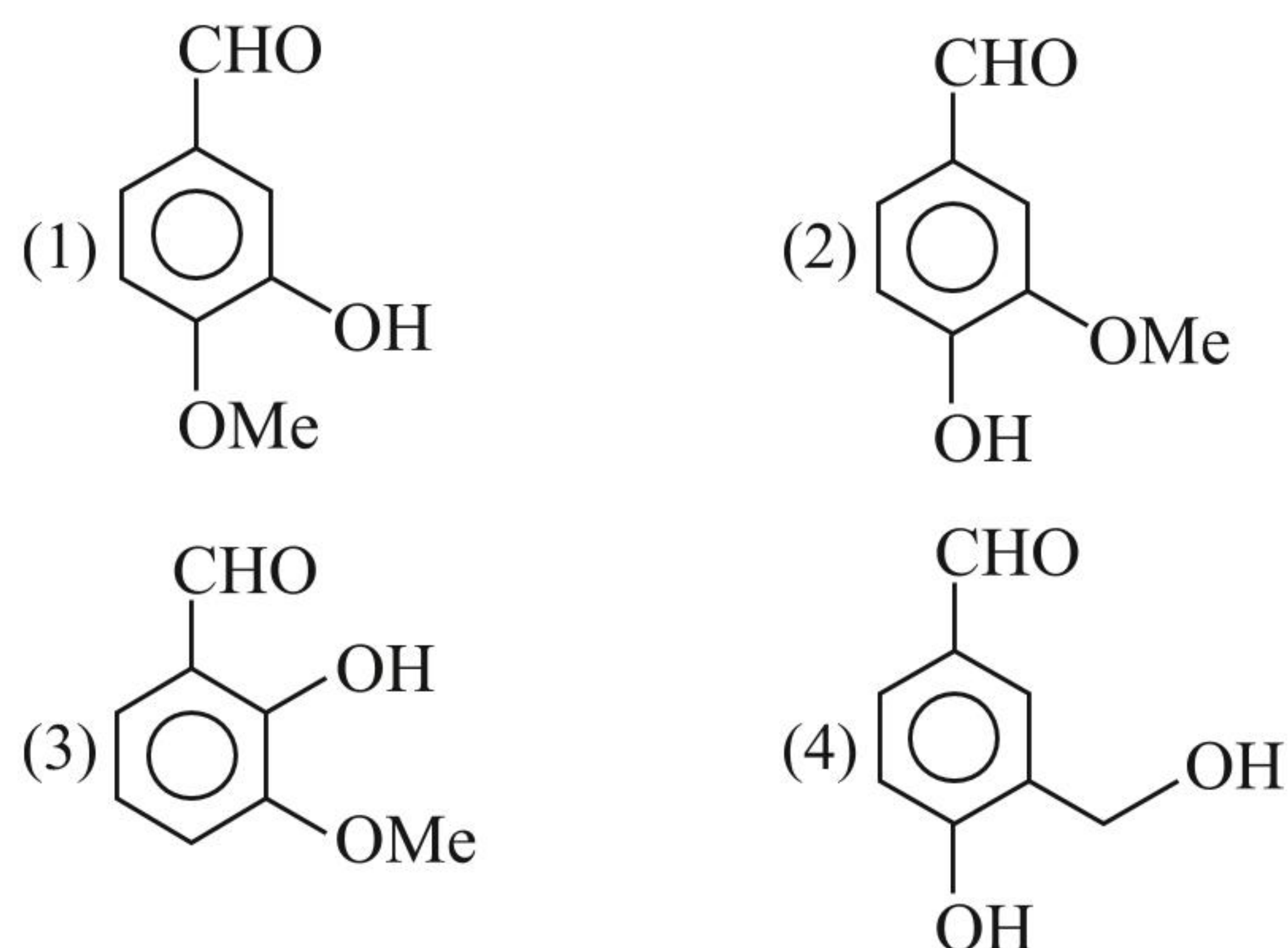
Linked Comprehension Type

Paragraph 1

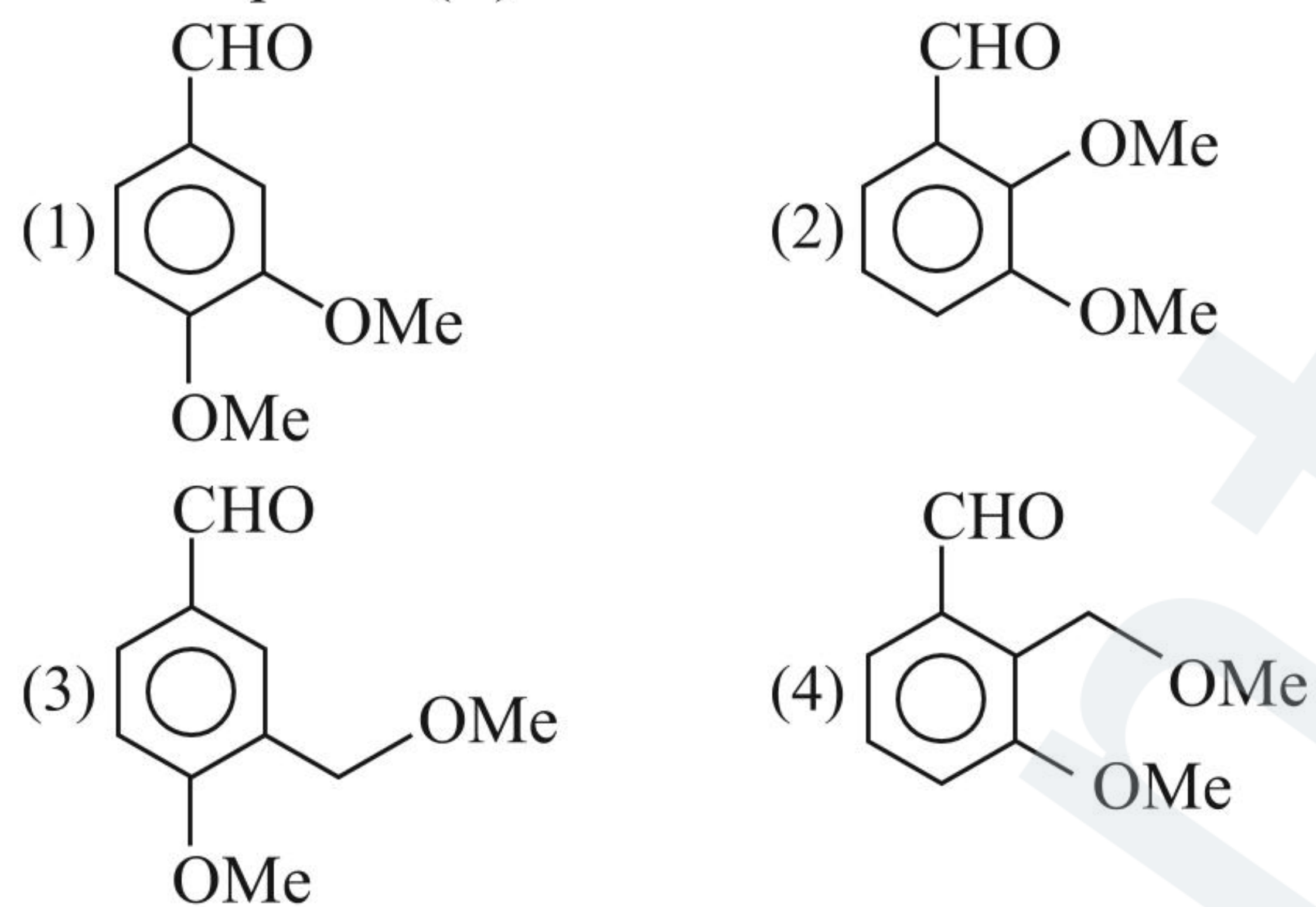




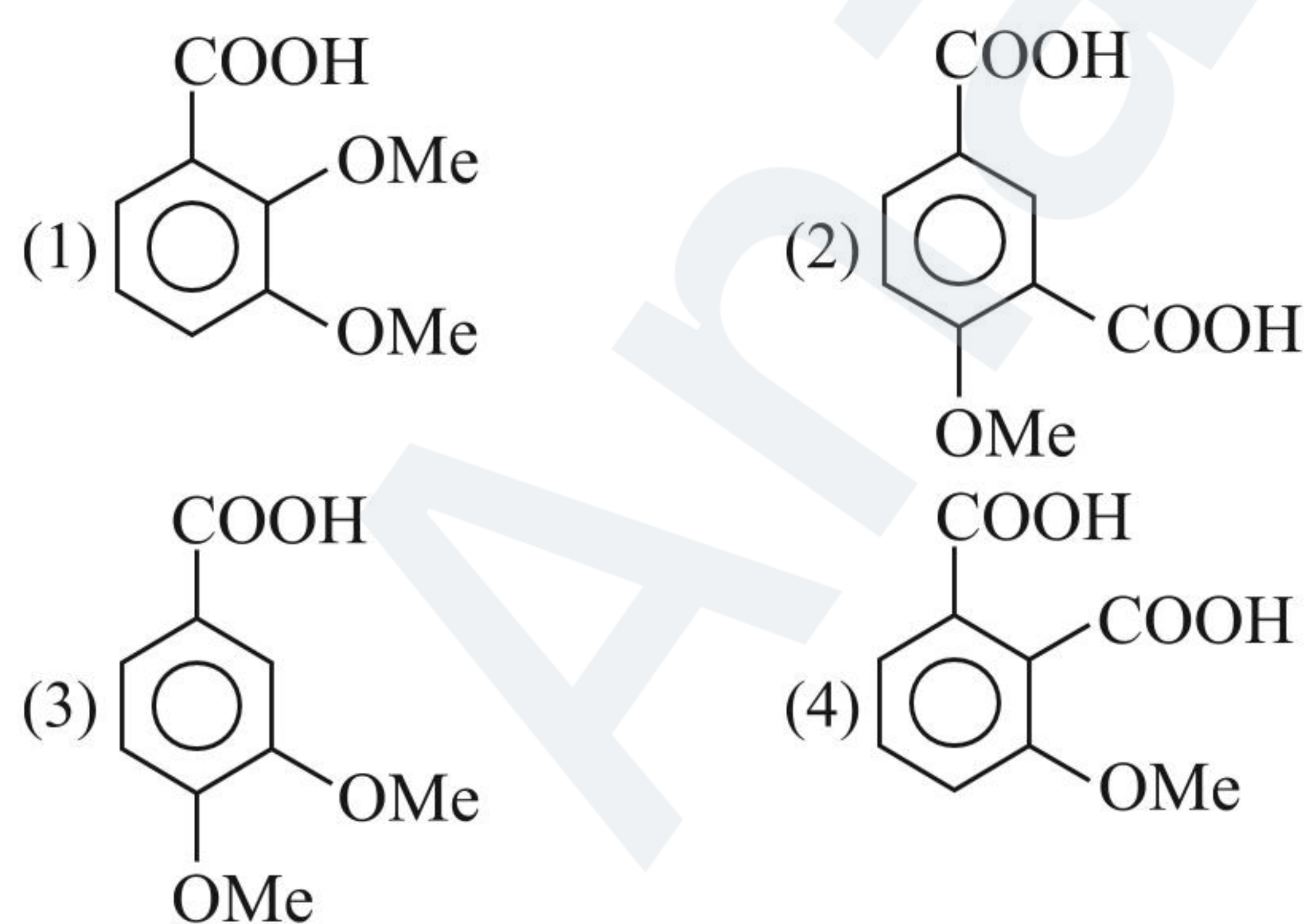
1. The compound (A) is:



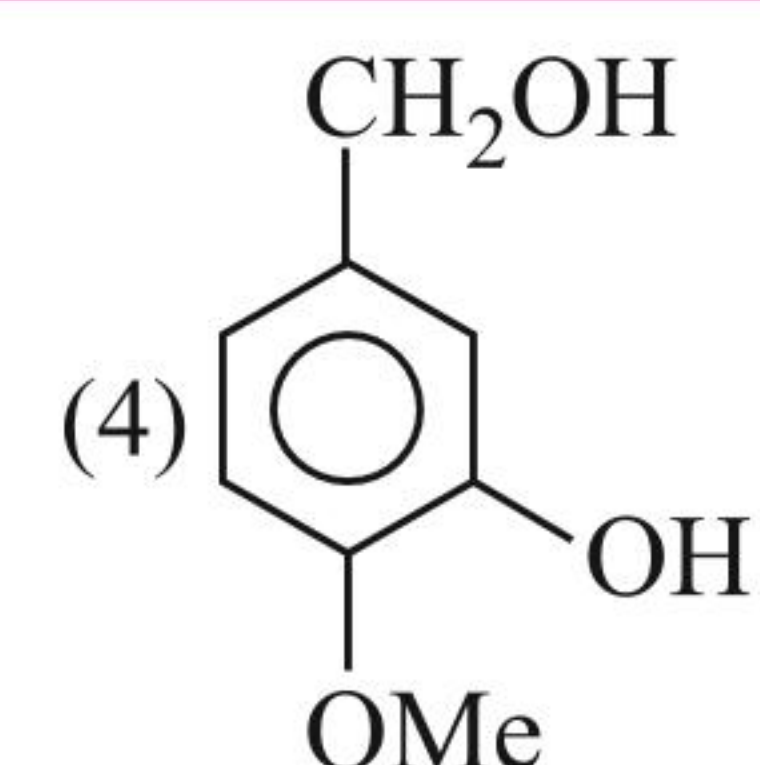
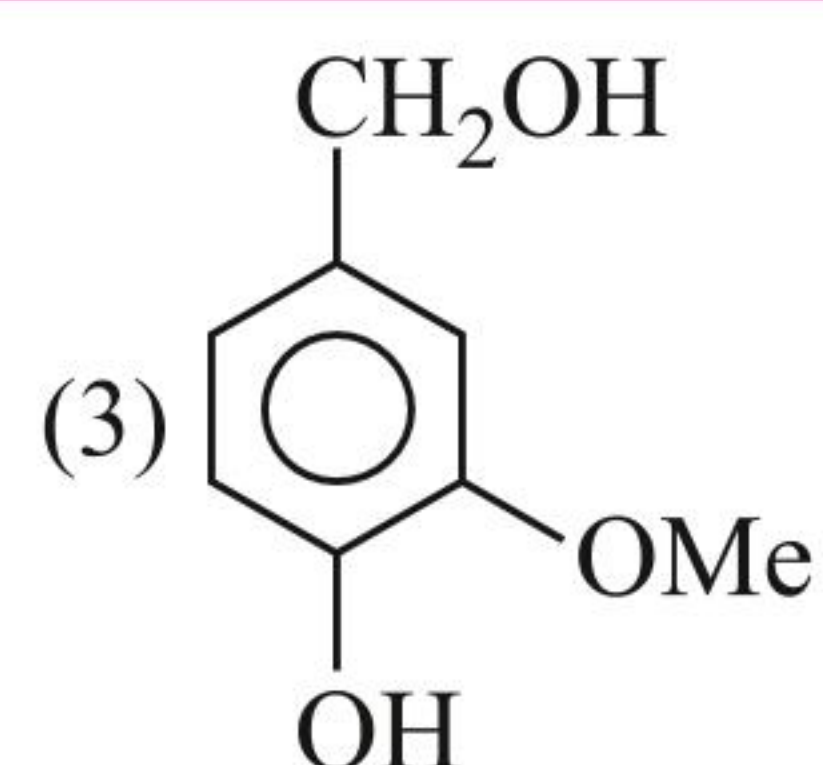
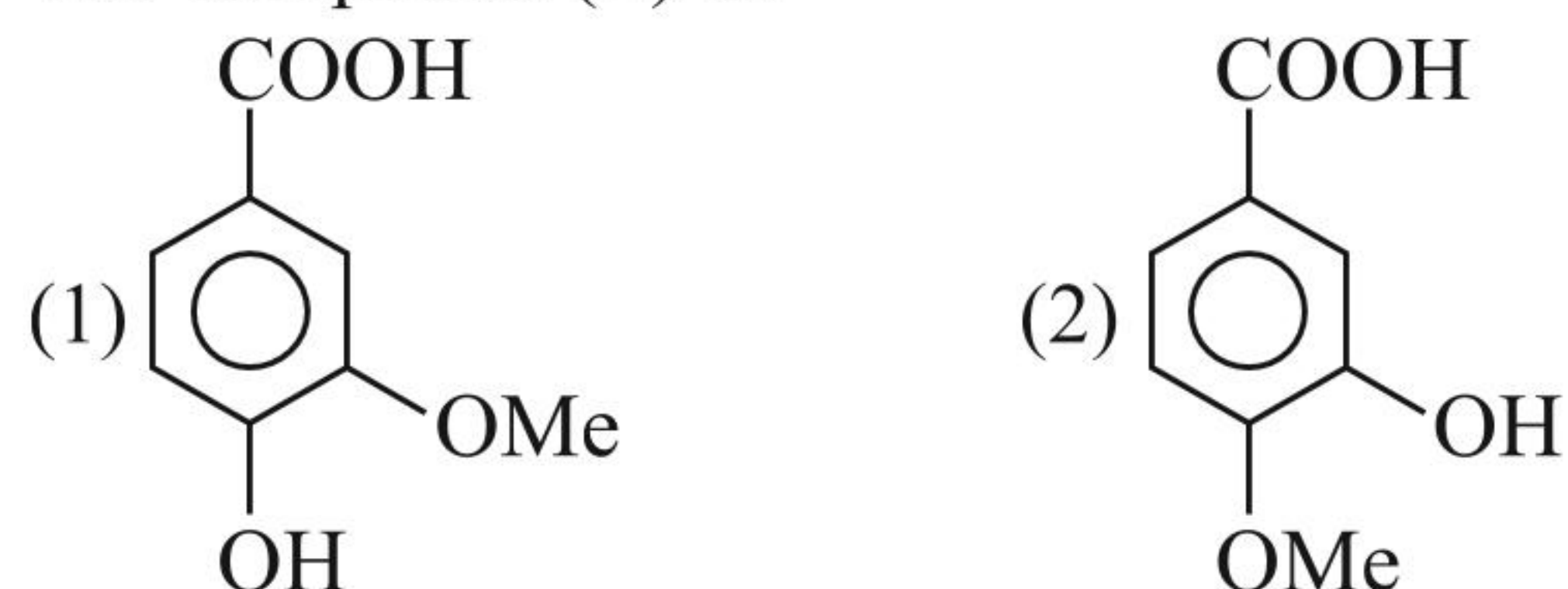
2. The compound (B) is:



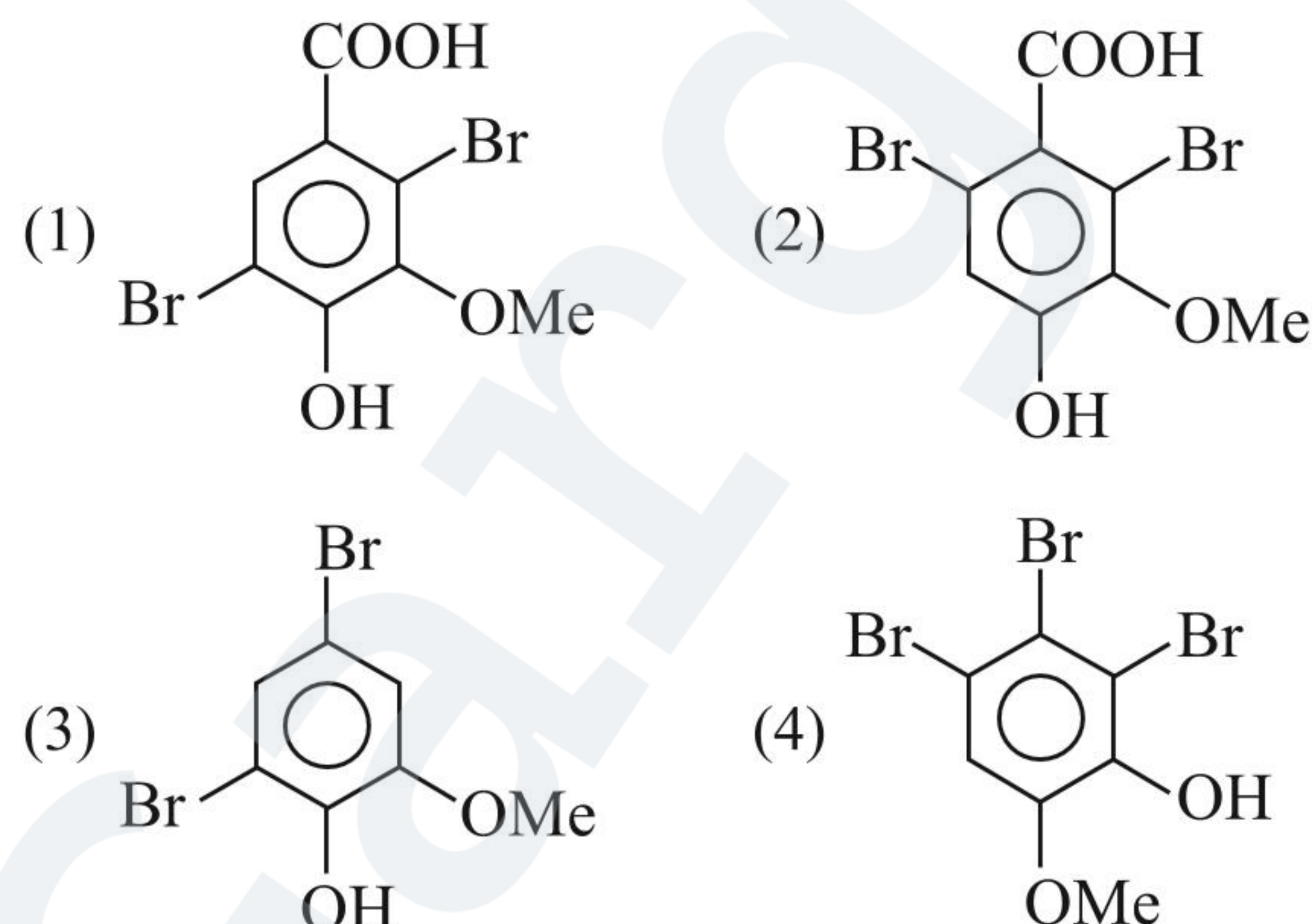
3. The compound (C) is:



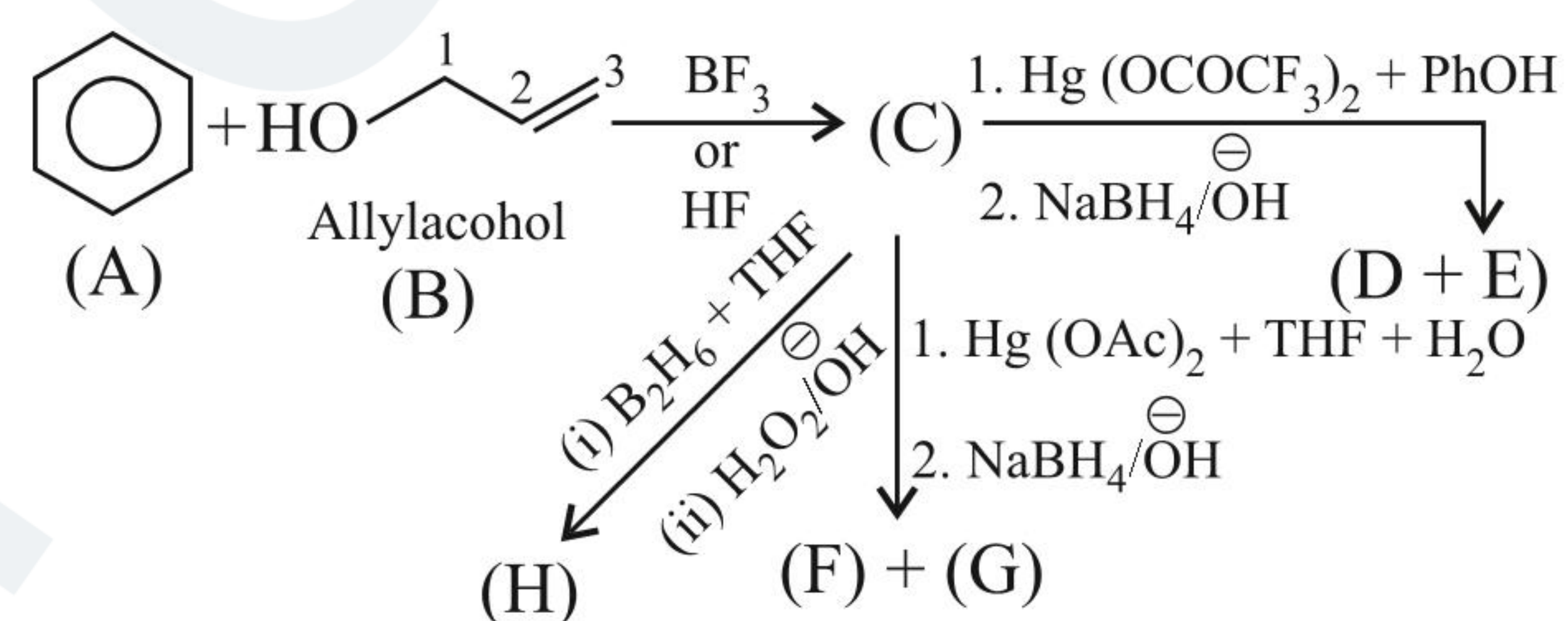
4. The compound (E) is:



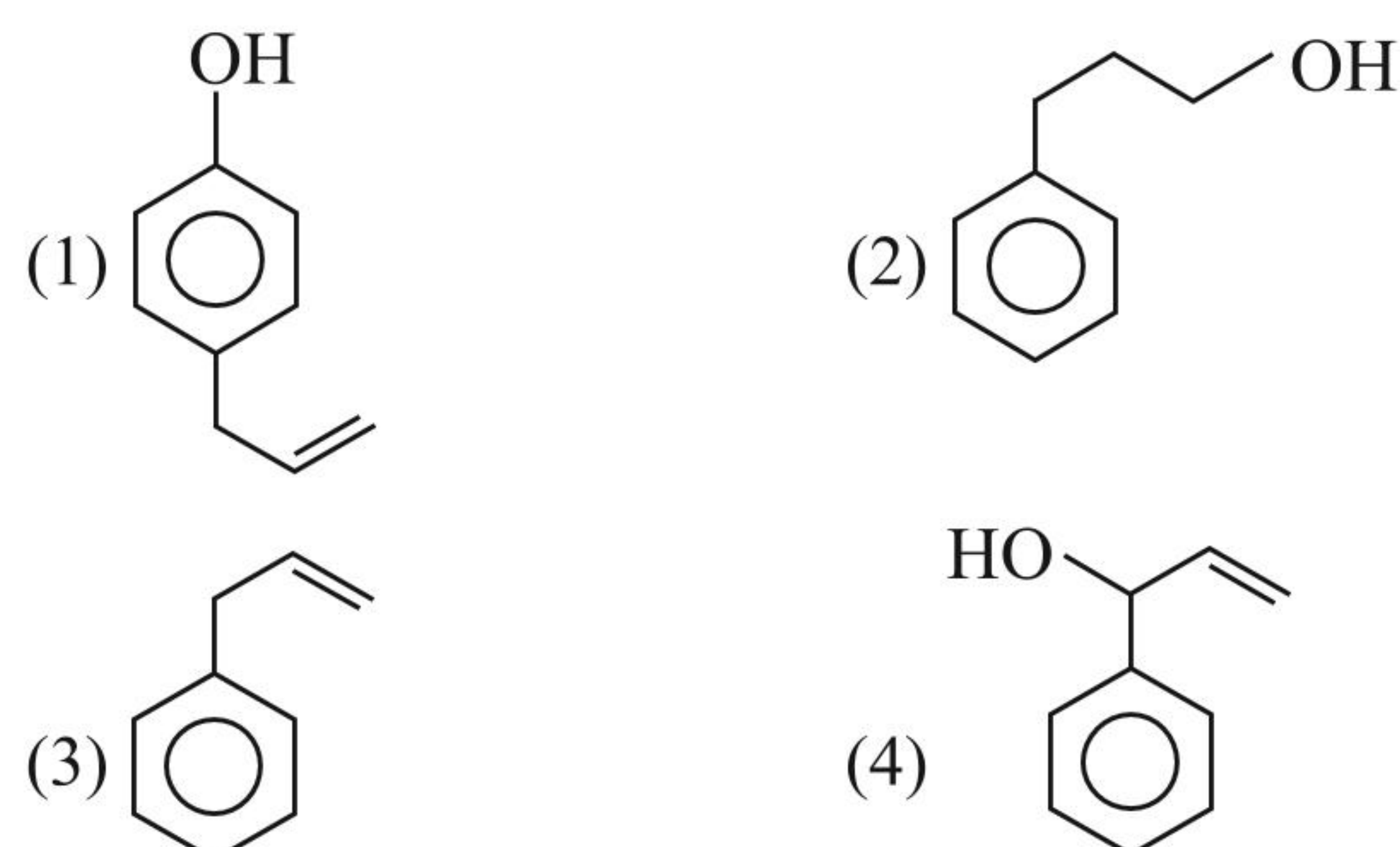
5. The compound (F) is:



Paragraph 2



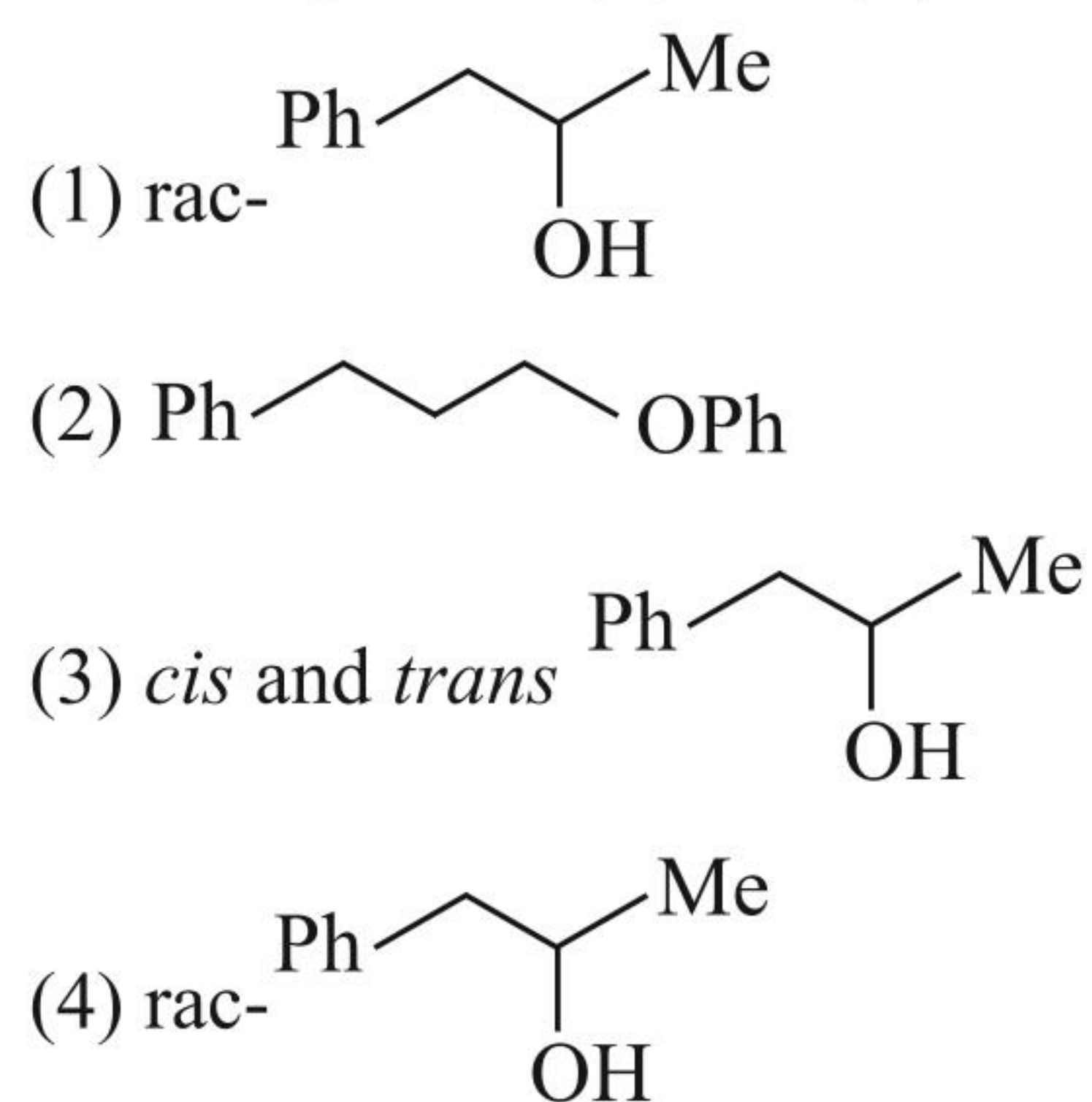
6. The compound (C) is:



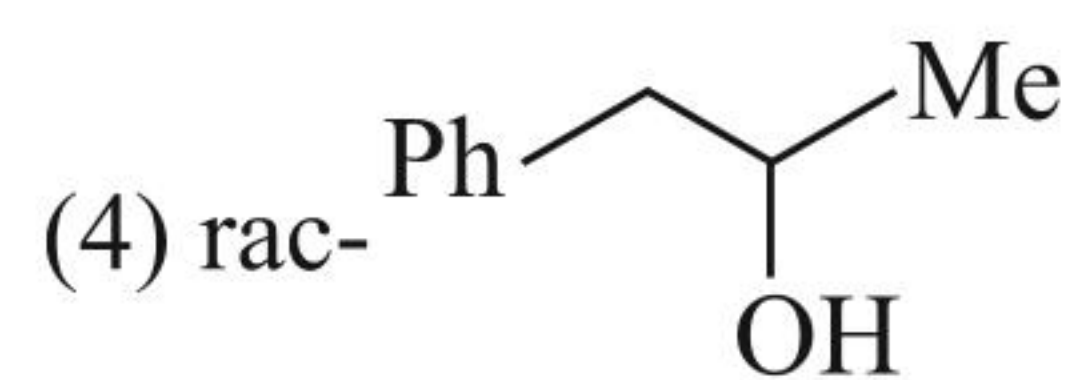
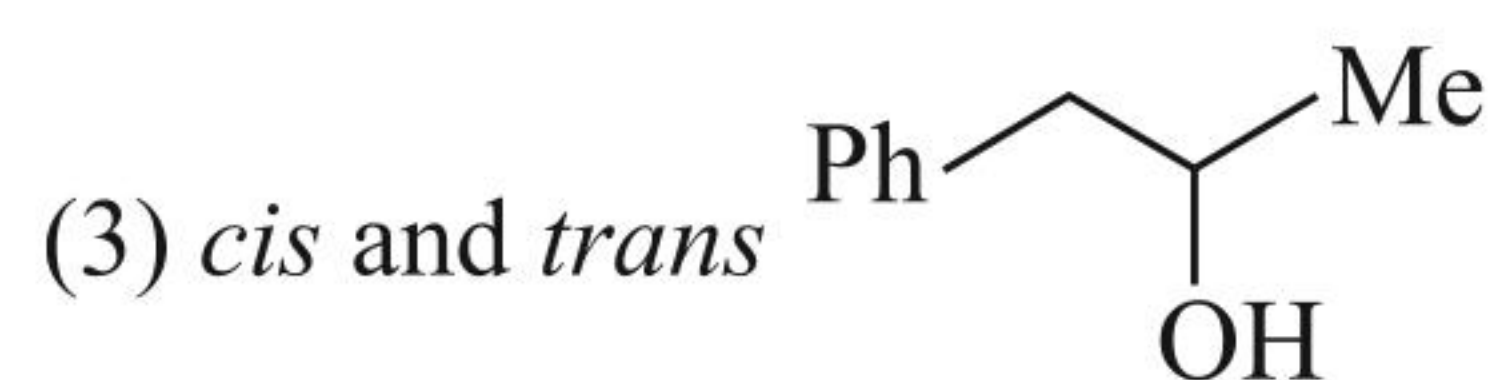
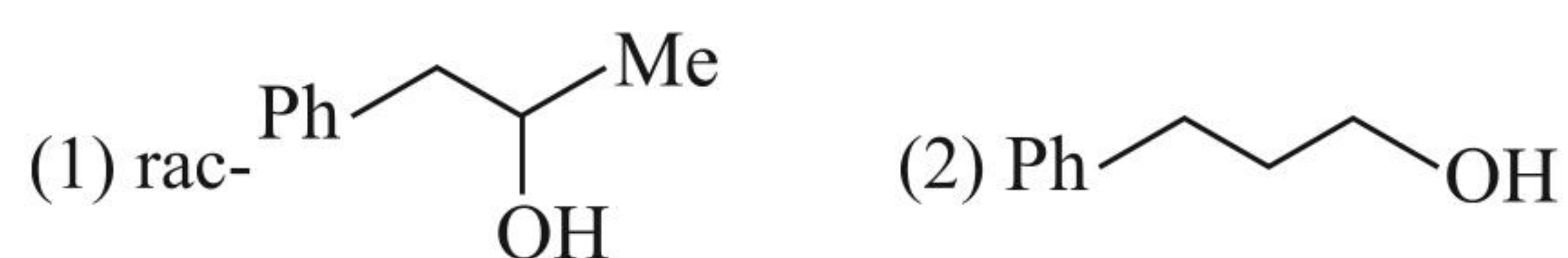
7. The compounds (D) and (E) are:

- (1) Enantiomers (2) Diastereomers
 (3) Geometrical isomers (4) Positional isomers

8. The compounds (D) and (E) are:



9. The compounds (F) and (G) are:



10. The compound (H) is:



(3) Both (1) and (2) (4) None

11. The reaction (C) to (D and E) is called alkoxy mercuriation-demercuration reaction. Which of the following statements, is wrong about the reaction?

- (1) In the first step, alkoxy mercuriation occurs, i.e., $\text{Hg}(\text{OAc})_2$ or $\text{Hg}(\text{OCOCF}_3)_2$ and ROH/ArOH add to the double bond.
- (2) In the second step, demercuration occurs, i.e., NaBH_4 reduces, HgOAc or $\text{Hg}(\text{OCOCF}_3)$ group to hydrogen.
- (3) The net reaction is addition of ROH/ArOH according to Markovnikov's rule.
- (4) Rearrangement takes place.

12. The reaction (C) to (F and G) is called mercuriation-demercuration reaction. Which of the following statements is wrong about the reaction?

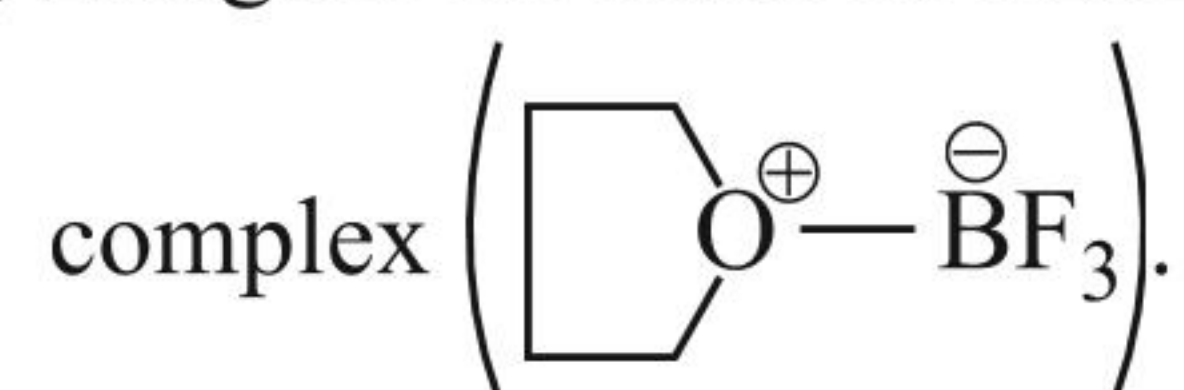
- (1) The reaction proceeds *via* the formation of mercurinium ion as an intermediate.
- (2) The electrophile is HgOAc^\oplus .
- (3) In the final step, Hg^{1+} is reduced to Hg^0 .
- (4) In the final step, Hg^{2+} is reduced to Hg^0 .

13. The reaction (C) to (H) is called hydroboration oxidation of alkene. Which statement is **true** about the reaction?

- (1) Anti-hydration of alkene occurs with a regioselectivity according to anti-Markovnikov's rule.
- (2) Syn-hydration (addition) of alkene and carbocation intermediate is involved.
- (3) The hydrogen atom that bonds to C atom comes from borane and the (OH) group from H_2O_2 .
- (4) The H atom that bonds to C atom comes from borane and (OH) group from the solvent (H_2O).

14. Which of the following statements is **wrong** about hydroboration oxidation?

- (1) The reaction proceeds through cyclic intermediate transition state and syn addition takes place.
- (2) Reagent diborane in ether (THF) exists as borane-THF



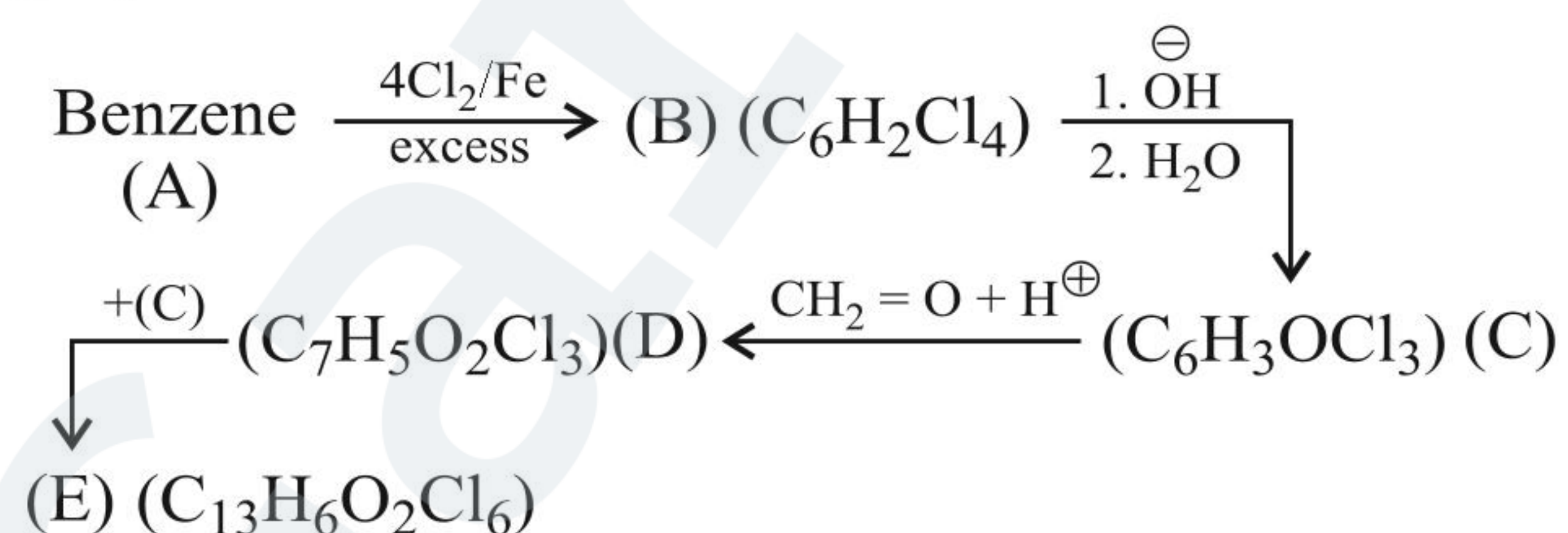
- (3) Diborane in polar solvent (H_2O) exists as $[\text{BH}_2]^\oplus [\text{BH}_4]^\ominus$.

(4) The reaction proceeds through ionic intermediate and syn addition takes place.

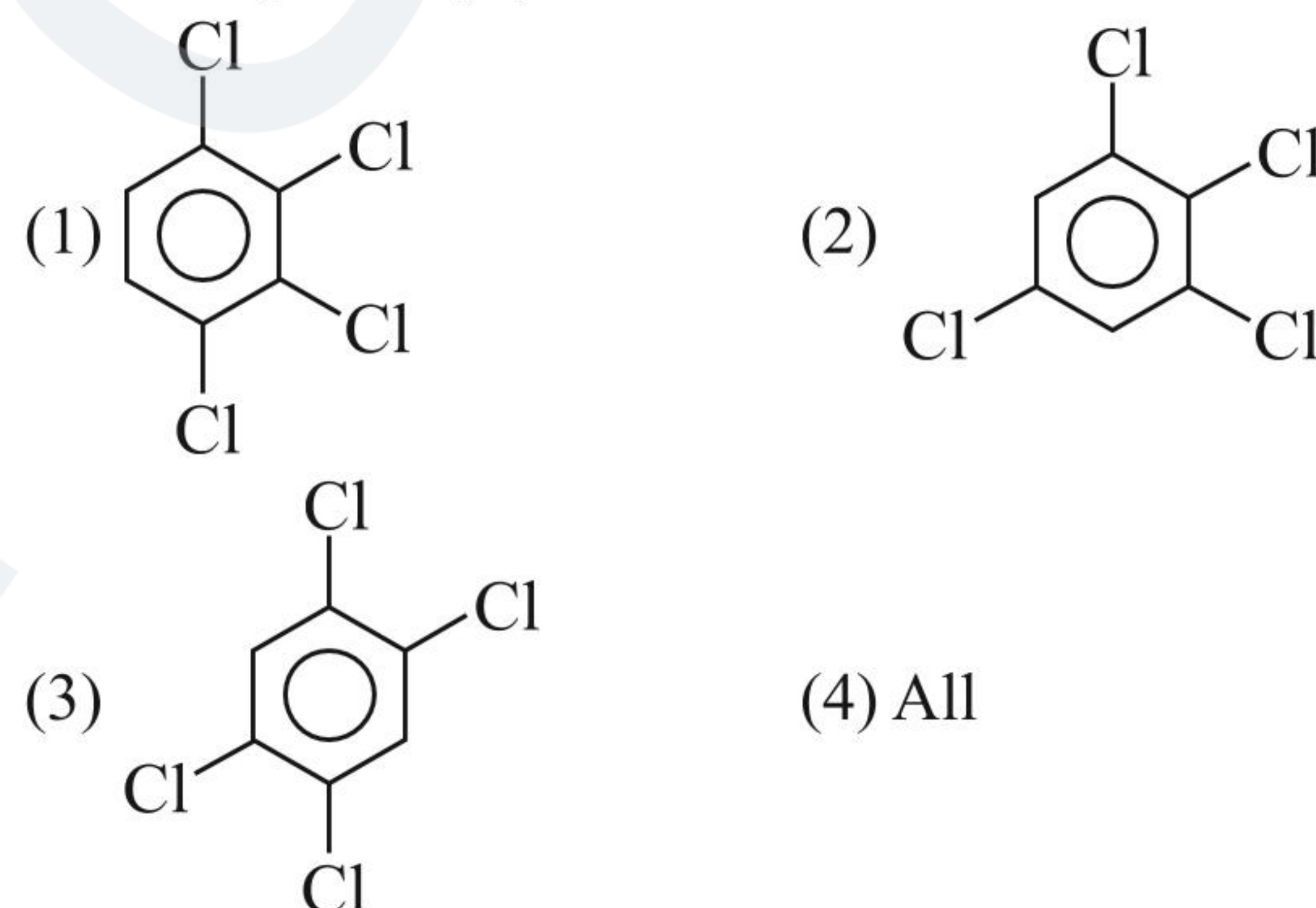
15. Which statement is **wrong** about alkoxy or mercuriation-demercuration reaction?

- (1) The first step, addition of electrophile (HgOAc^\oplus) to alkene, is stereospecific.
- (2) The second step, demercuration step, addition of H atom, is with no clear stereospecificity.
- (3) The net reaction is non-stereospecific.
- (4) The net reaction is stereospecific.

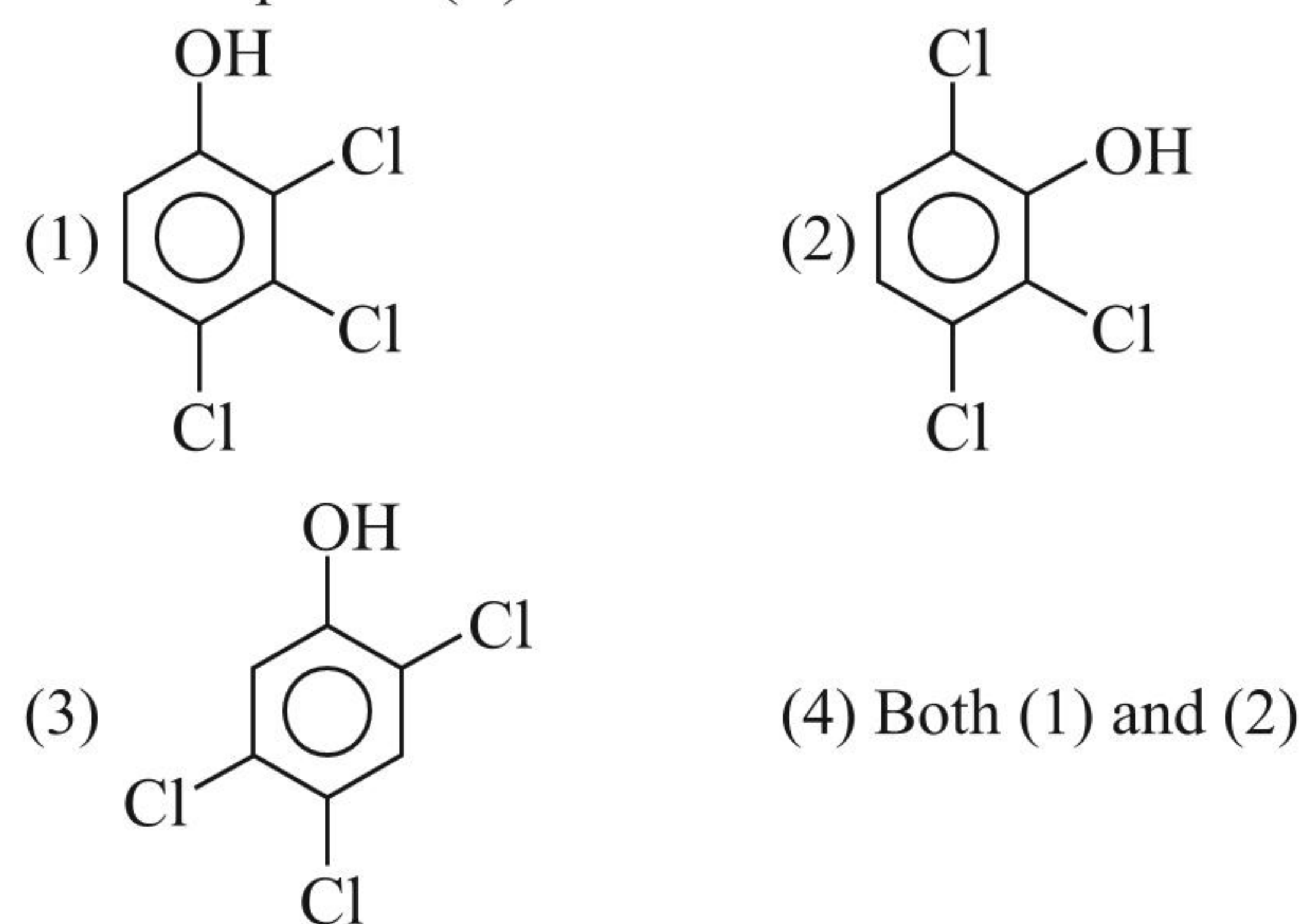
Paragraph 3



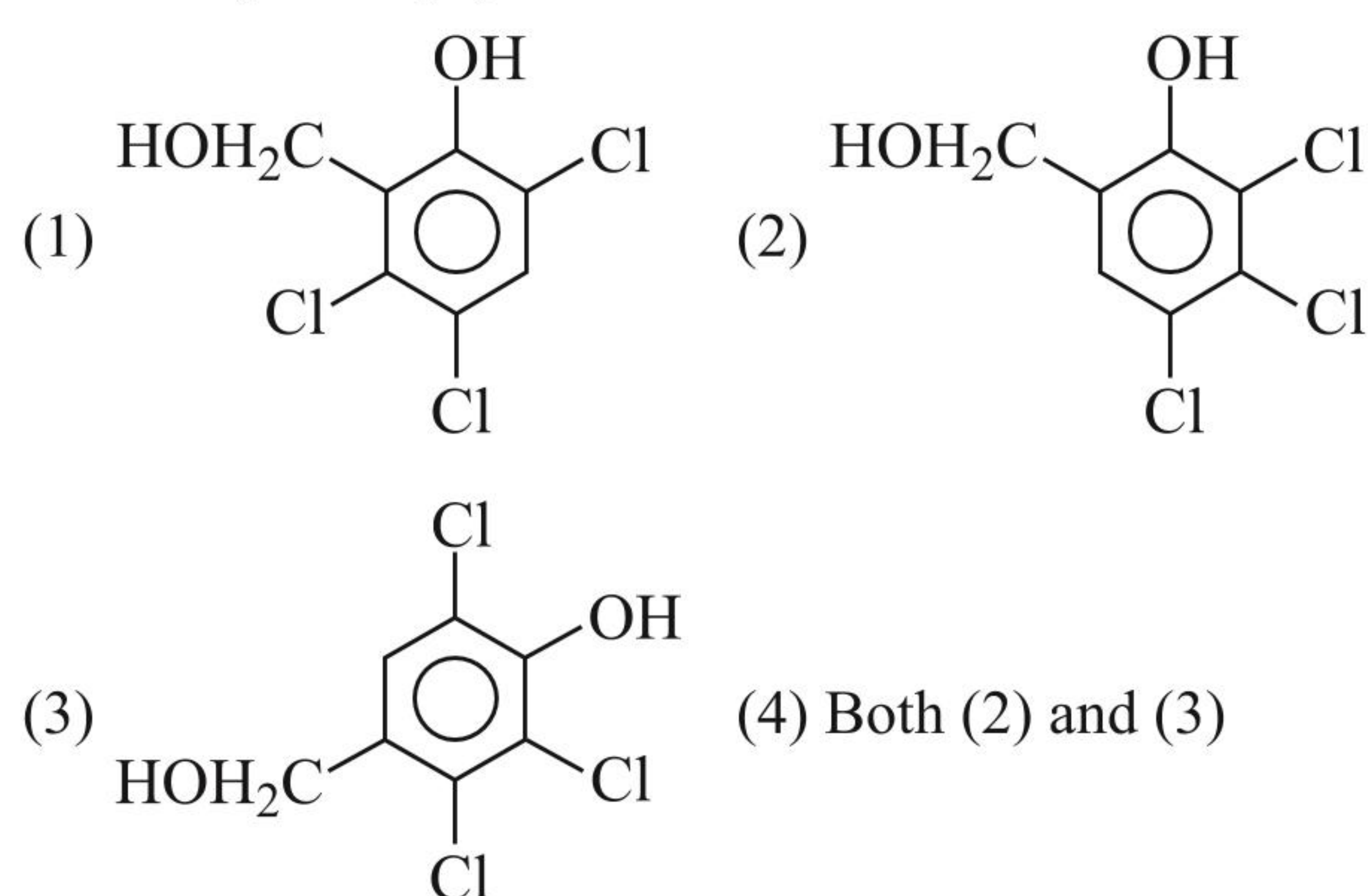
16. The compound (B) is:



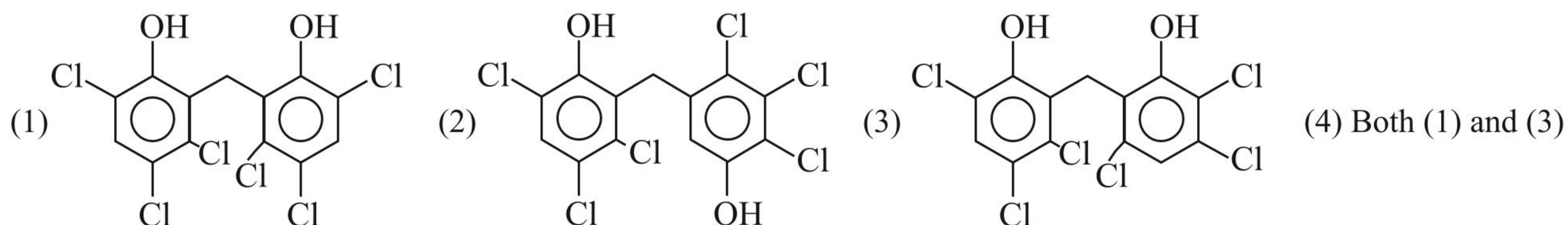
17. The compound (C) is:



18. The compound (D) is:

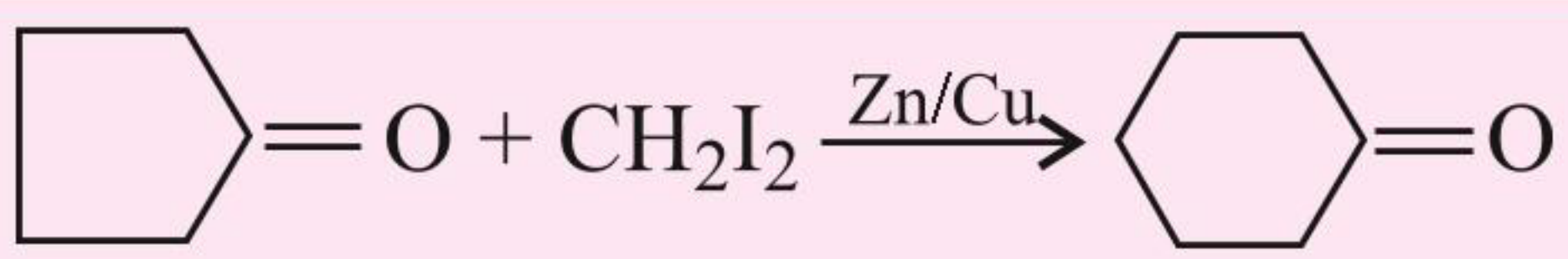

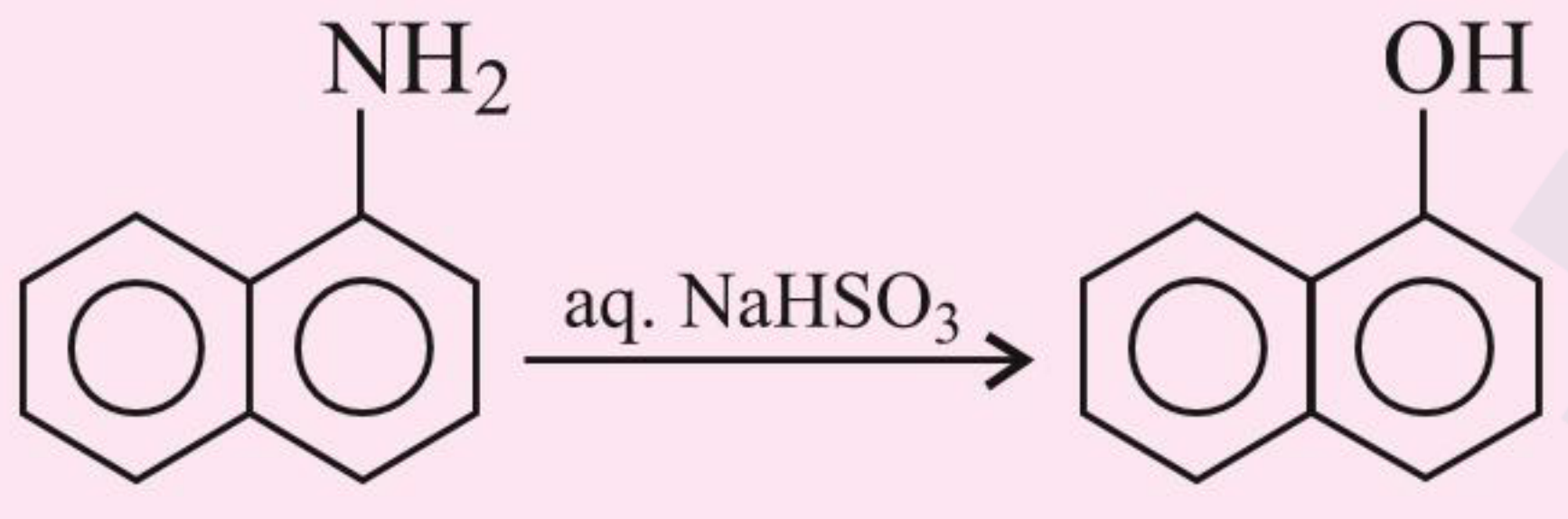


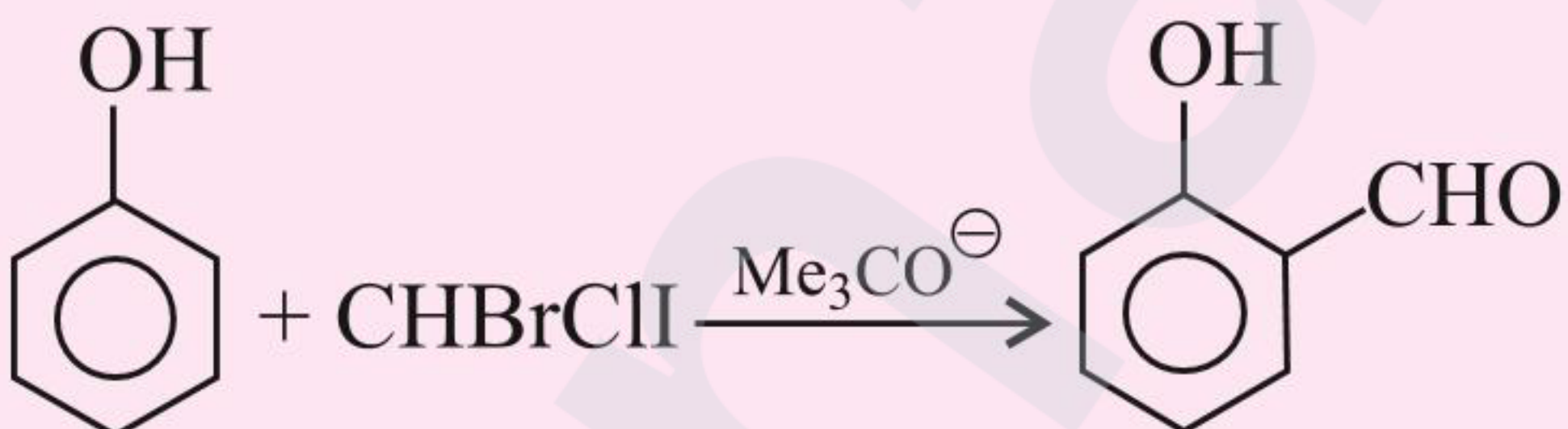
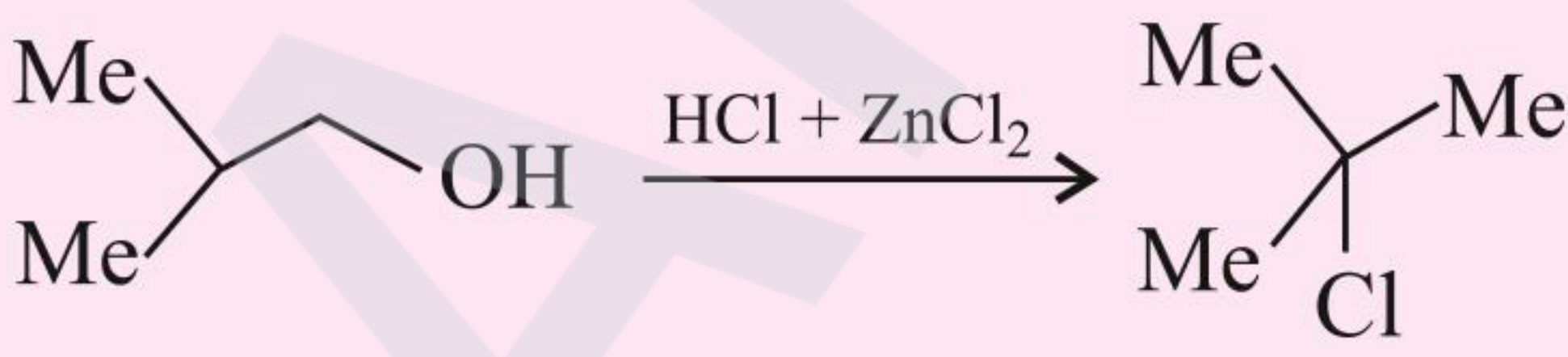
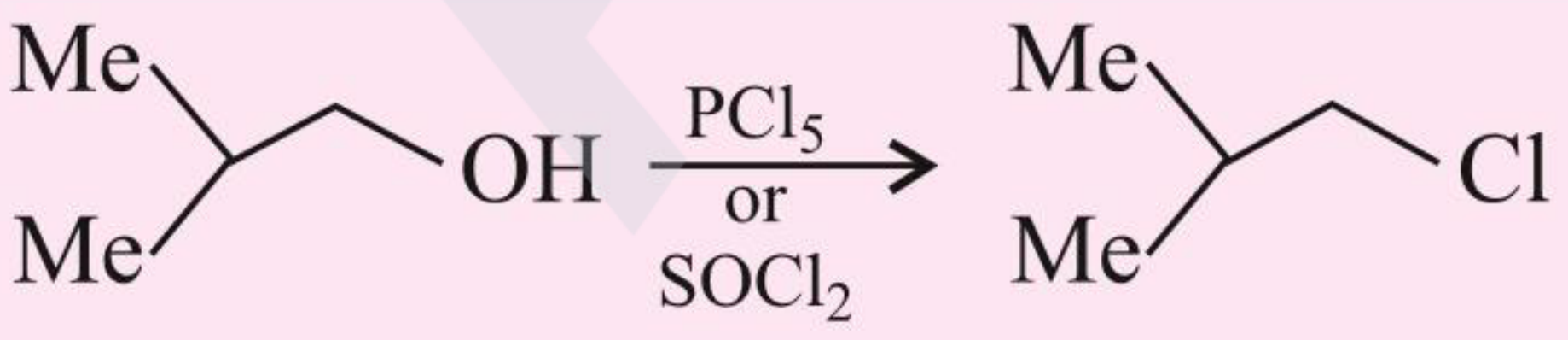
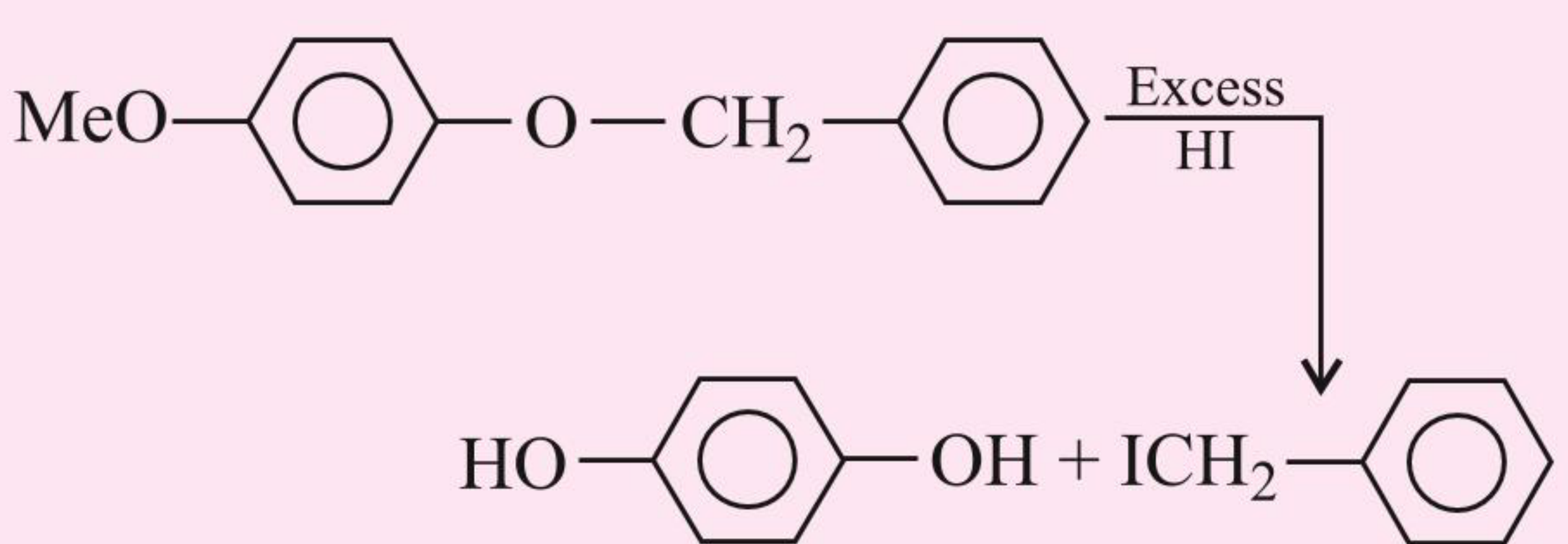
19. The compound (E) is:

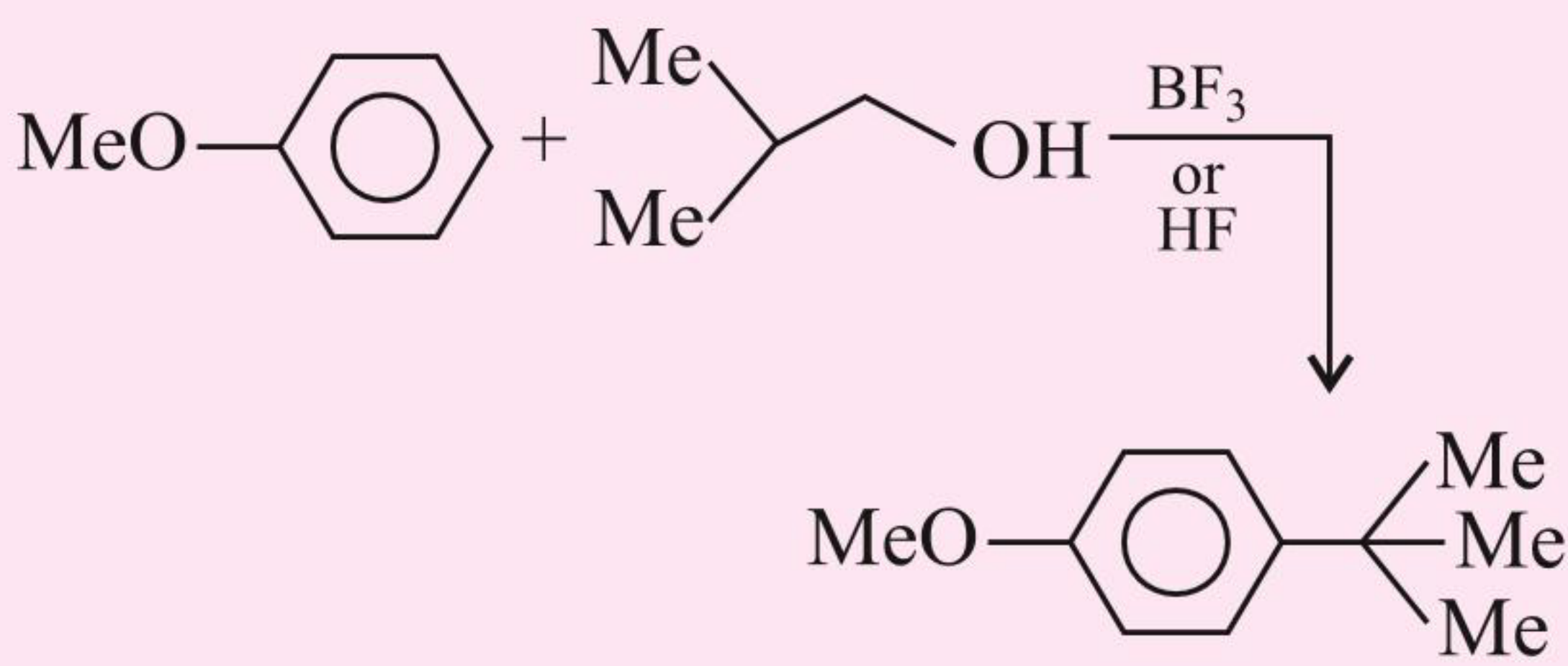



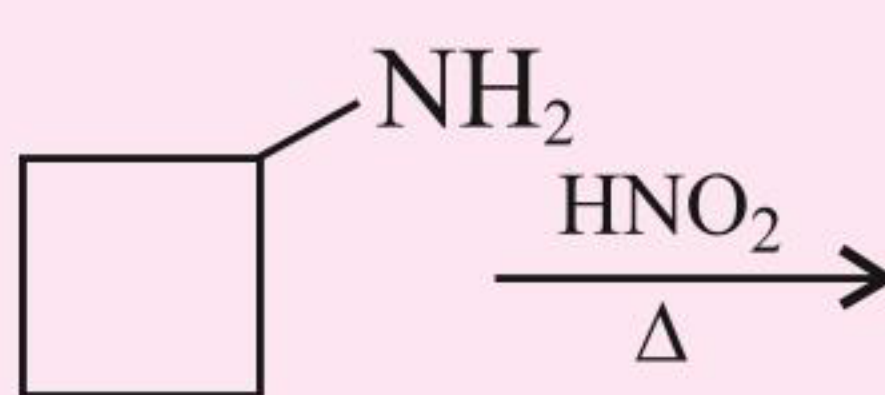
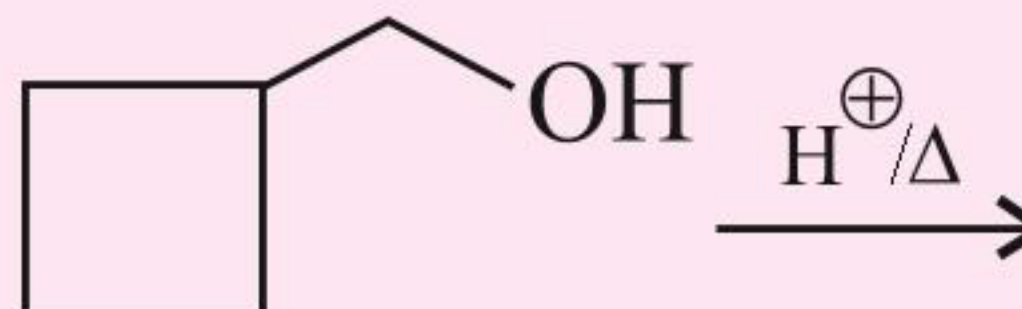
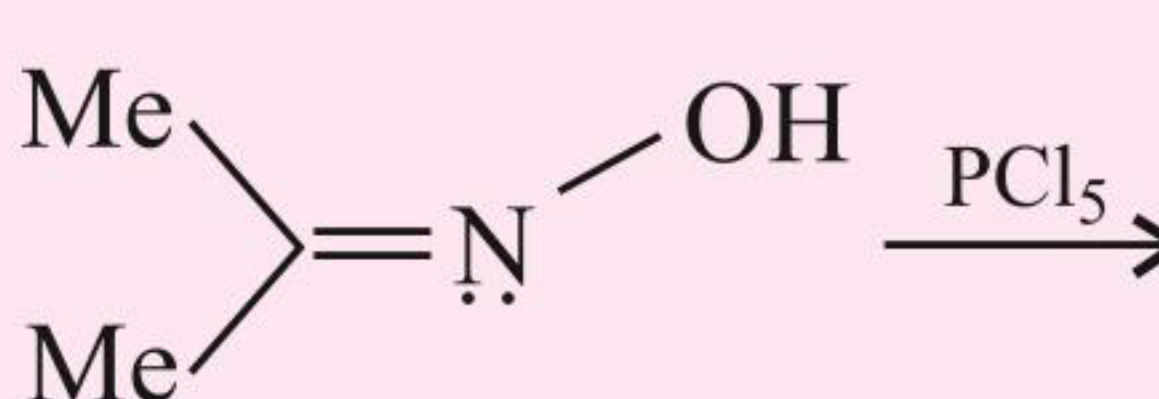
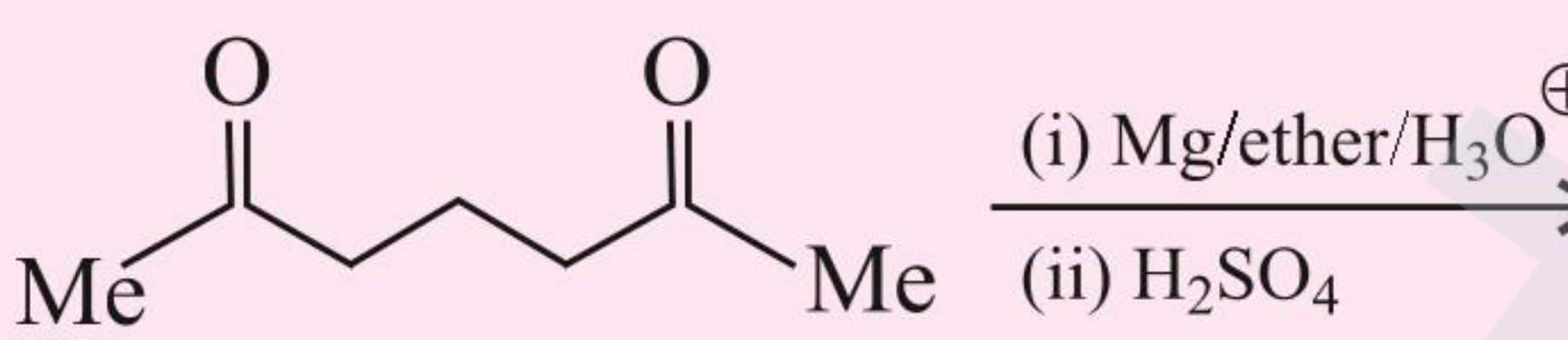
Matrix Match Type

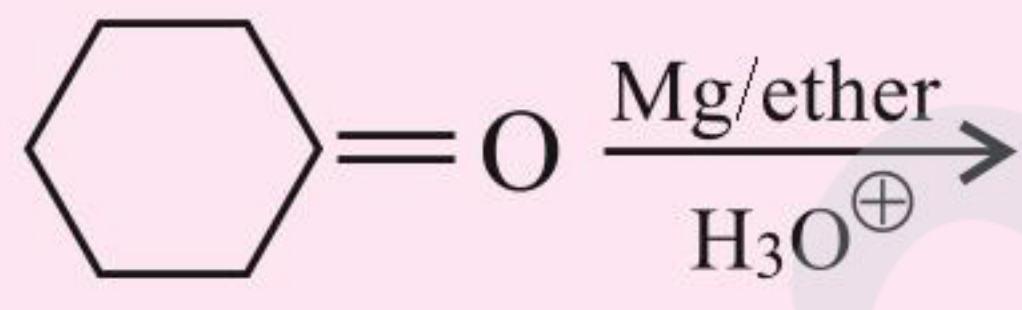

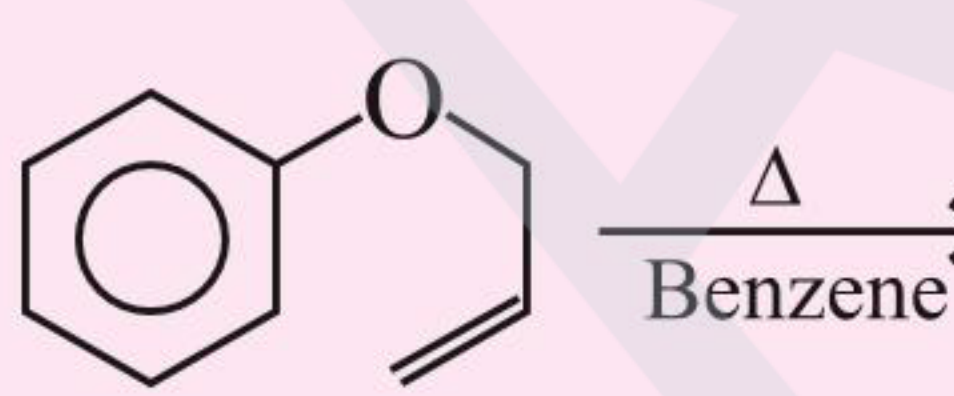
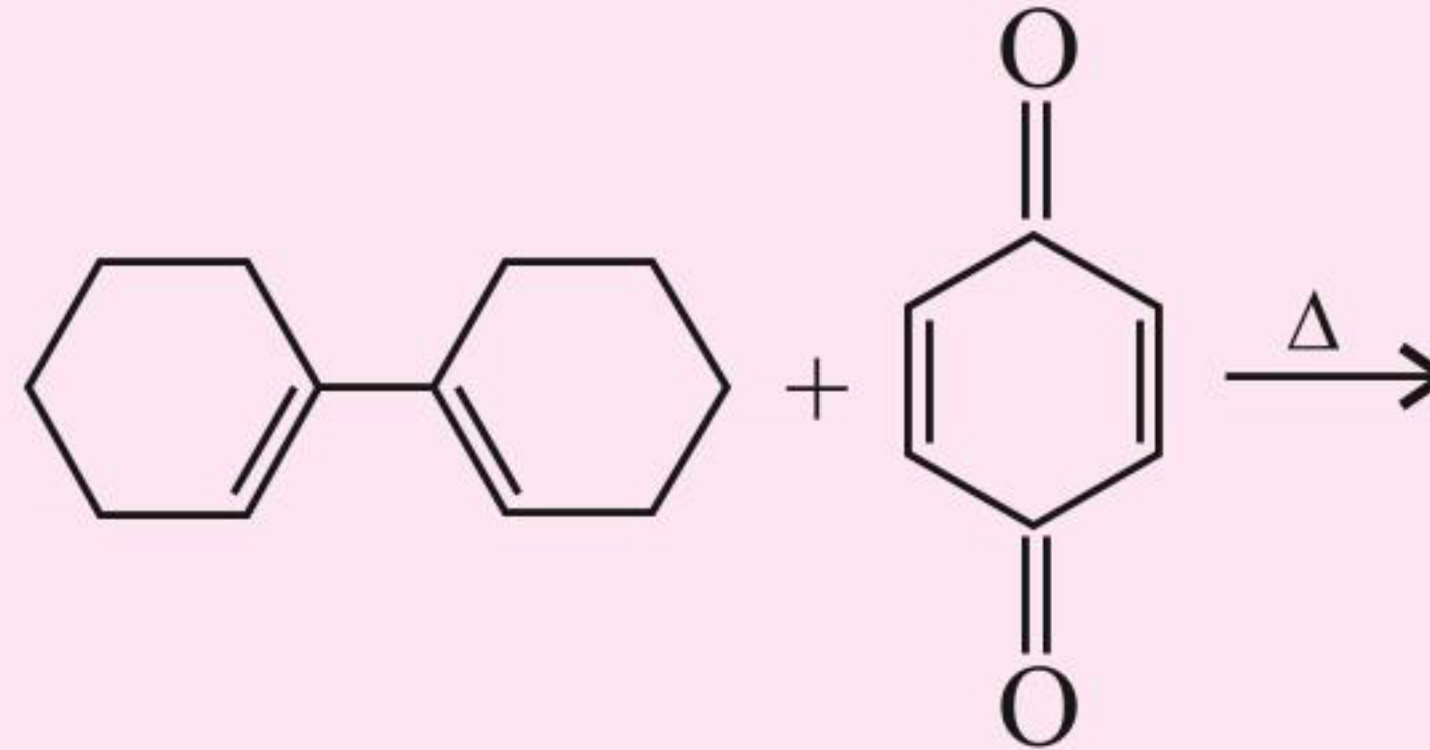
Match the compounds in Column I with their characteristics/tests/reactions(s)/reagent(s)/stereochemistry/isomer(s) given in Column II. Matching can be one or more than one.

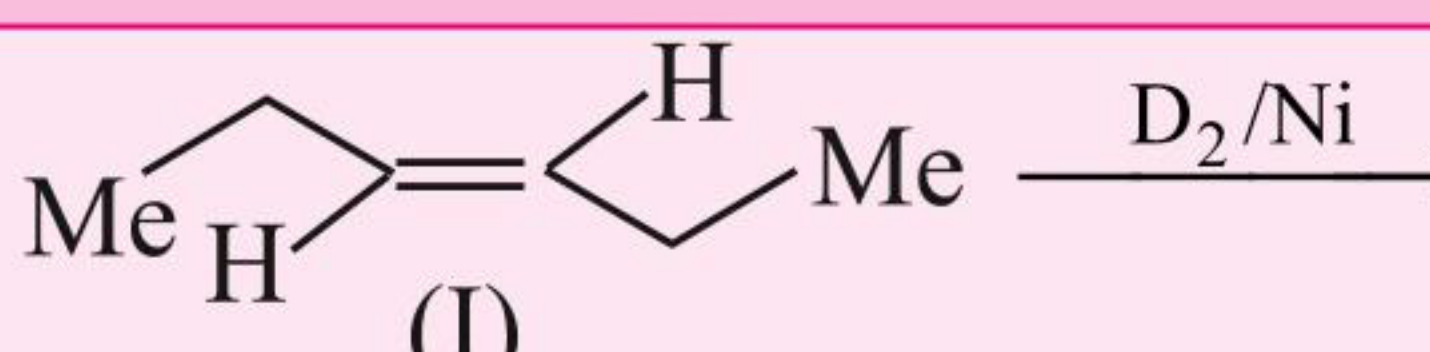
1.	Column I		Column II
	Reaction		Name of the reaction
a.	$\text{PhCOOAg} + \text{Br}_2 \xrightarrow[\Delta]{\text{CCl}_4} \text{PhBr} + \text{CO}_2 + \text{AgBr}$	p.	Simmons–Smith reactions
b.	$\text{C}_2\text{H}_5\text{COOAg} + \text{I}_2 \longrightarrow \text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + 2\text{AgI}$	q.	Borodine–Hunsdiecker reaction
c.		r.	Birnbaum–Simonini reaction
d.		s.	Carbene
e.		t.	Bischler–Napieralski reactions
		u.	Bucherer reaction

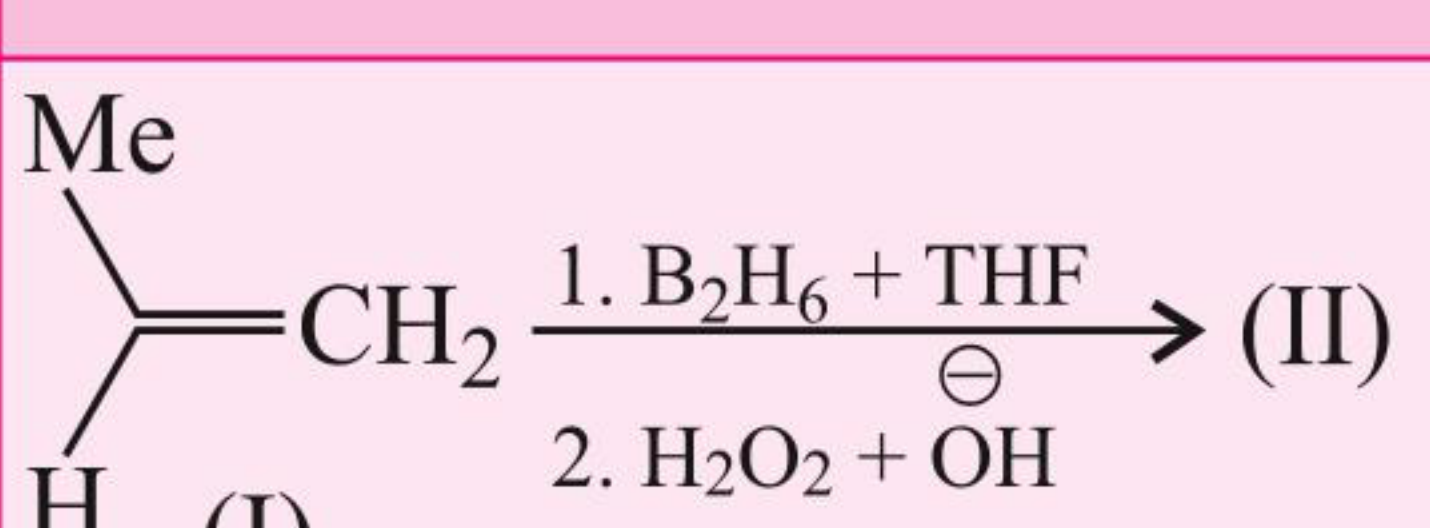

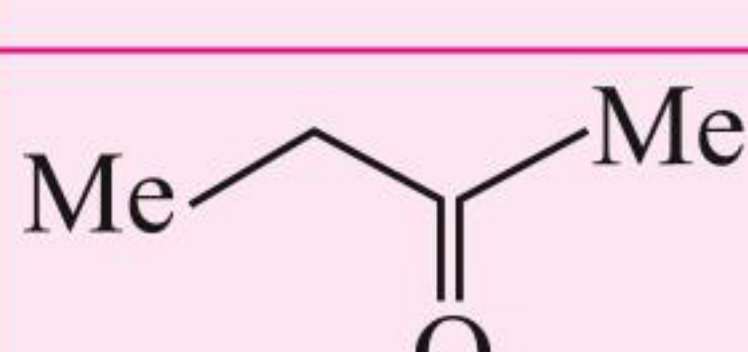
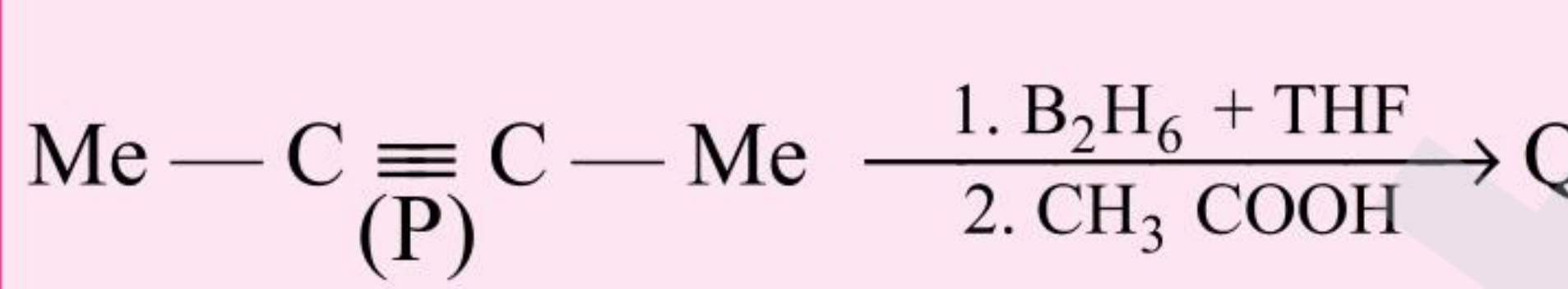
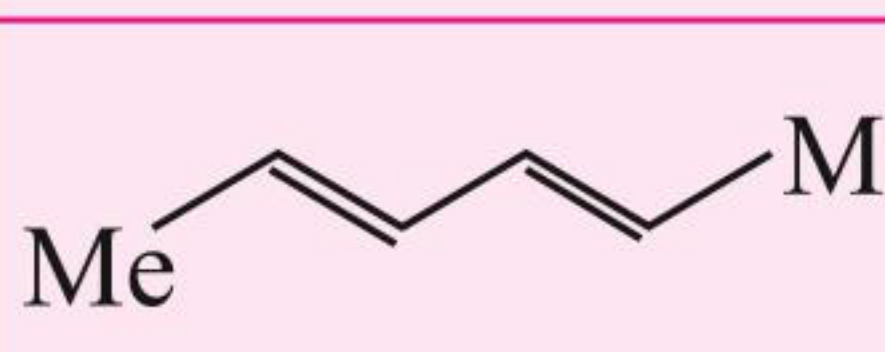
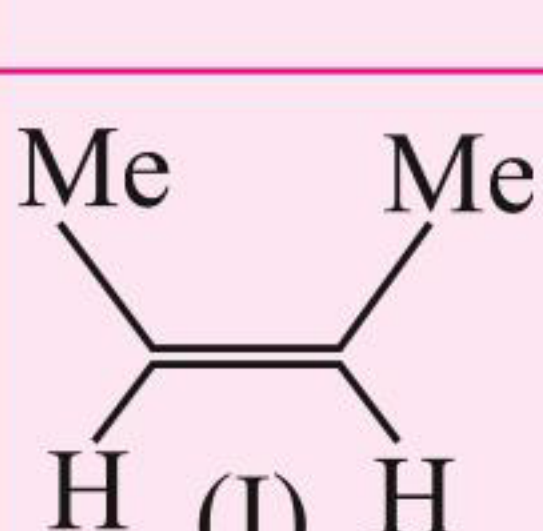

2.	Column I		Column II
	Reactions		Mechanism
a.		p.	Carbocation intermediate
b.		q.	Bromochloro carbene intermediate
c.		r.	SE reaction
d.		s.	Rearrangement of carbocation intermediate

e.		t.	S _N 1 mechanism
f.		u.	No rearrangement

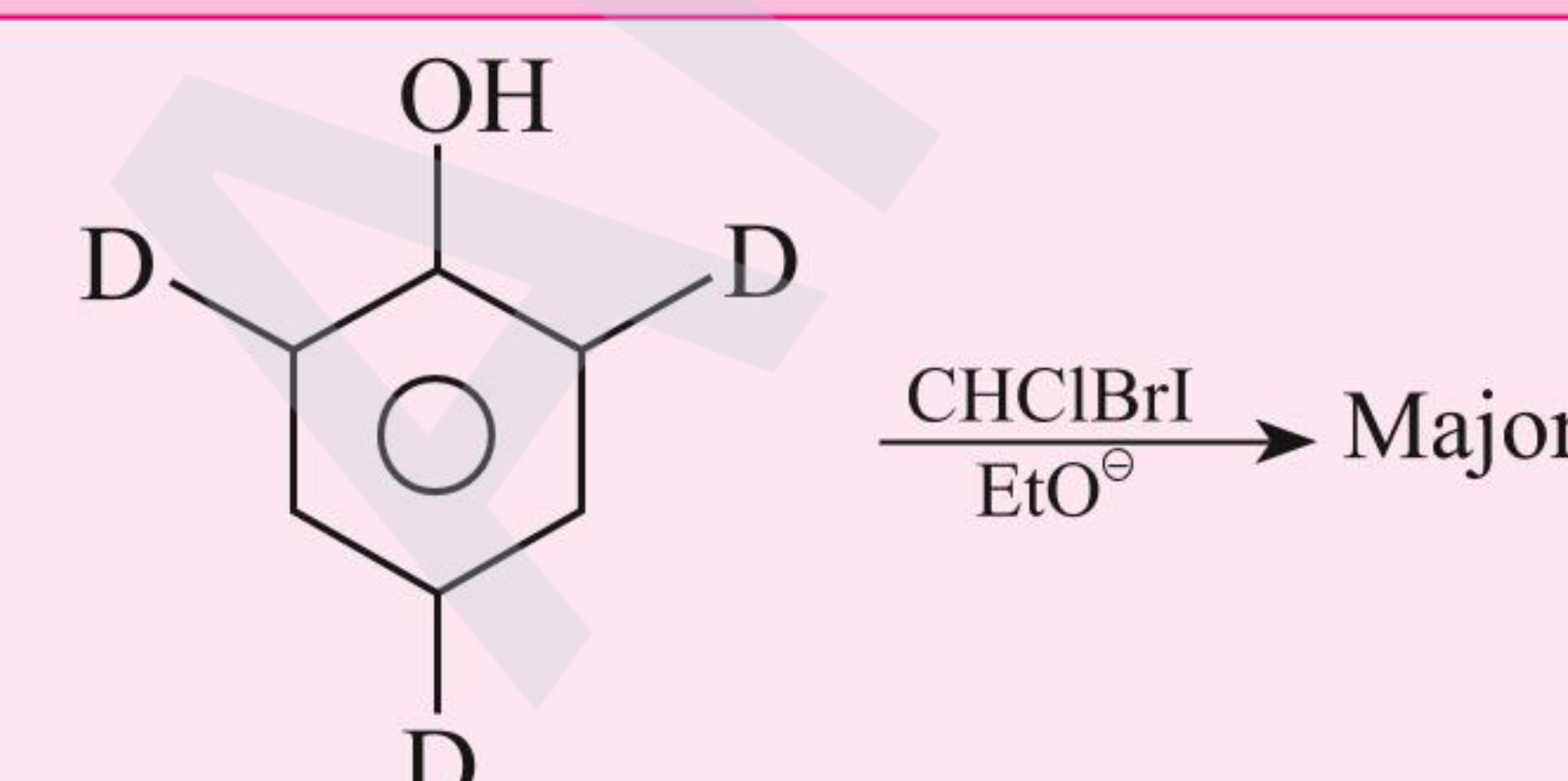
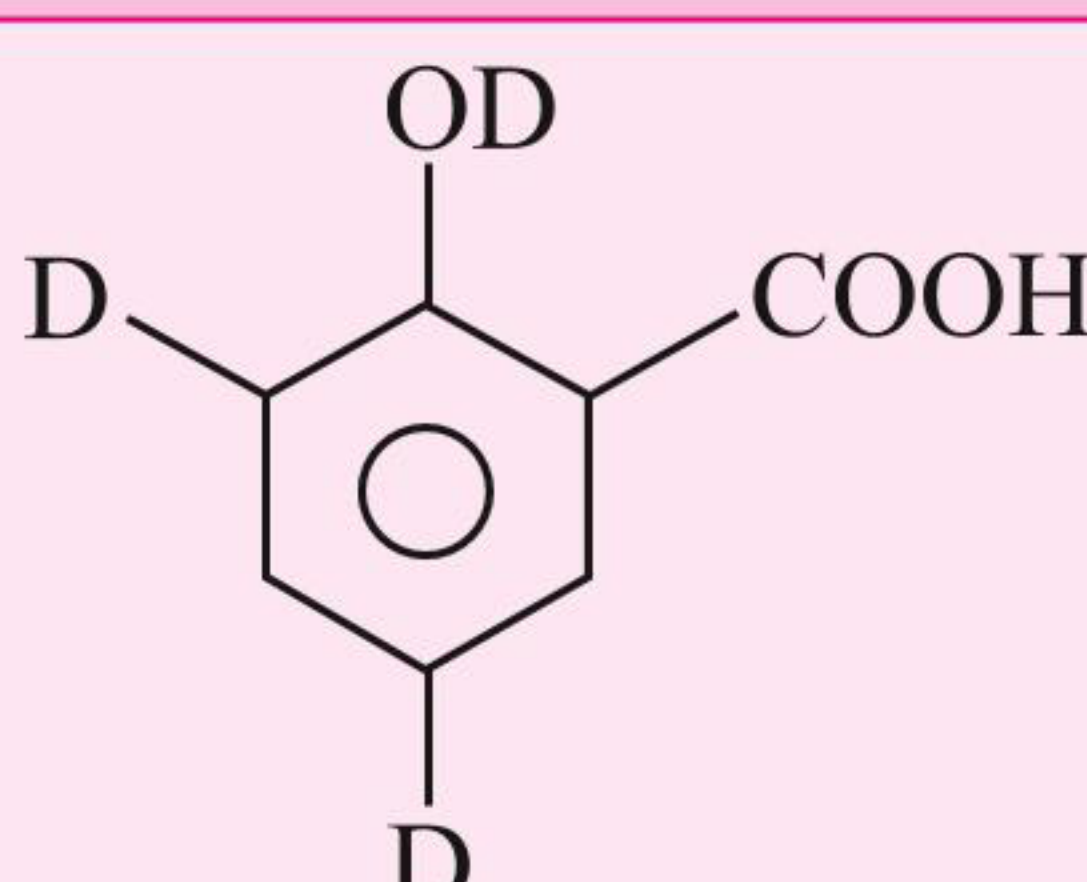
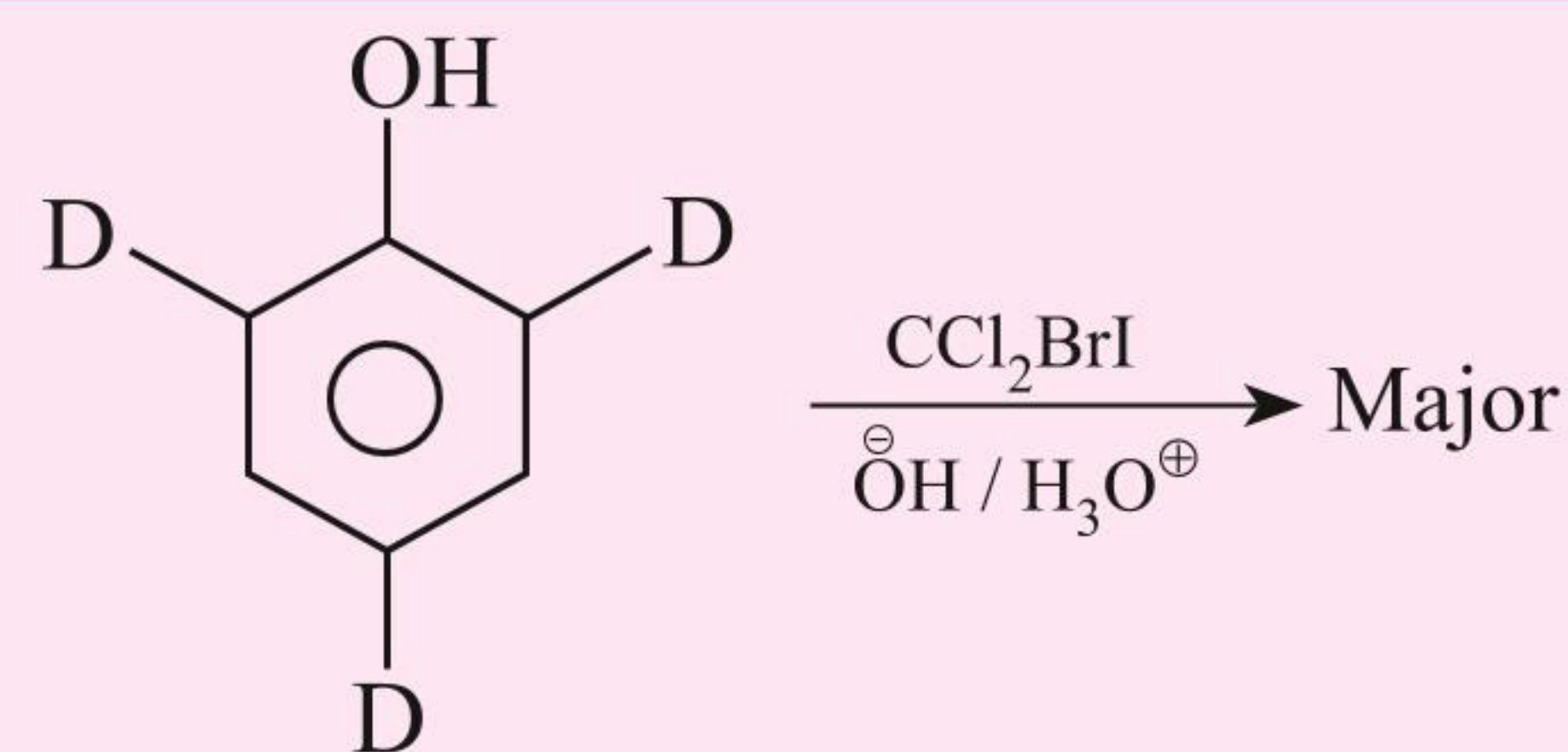
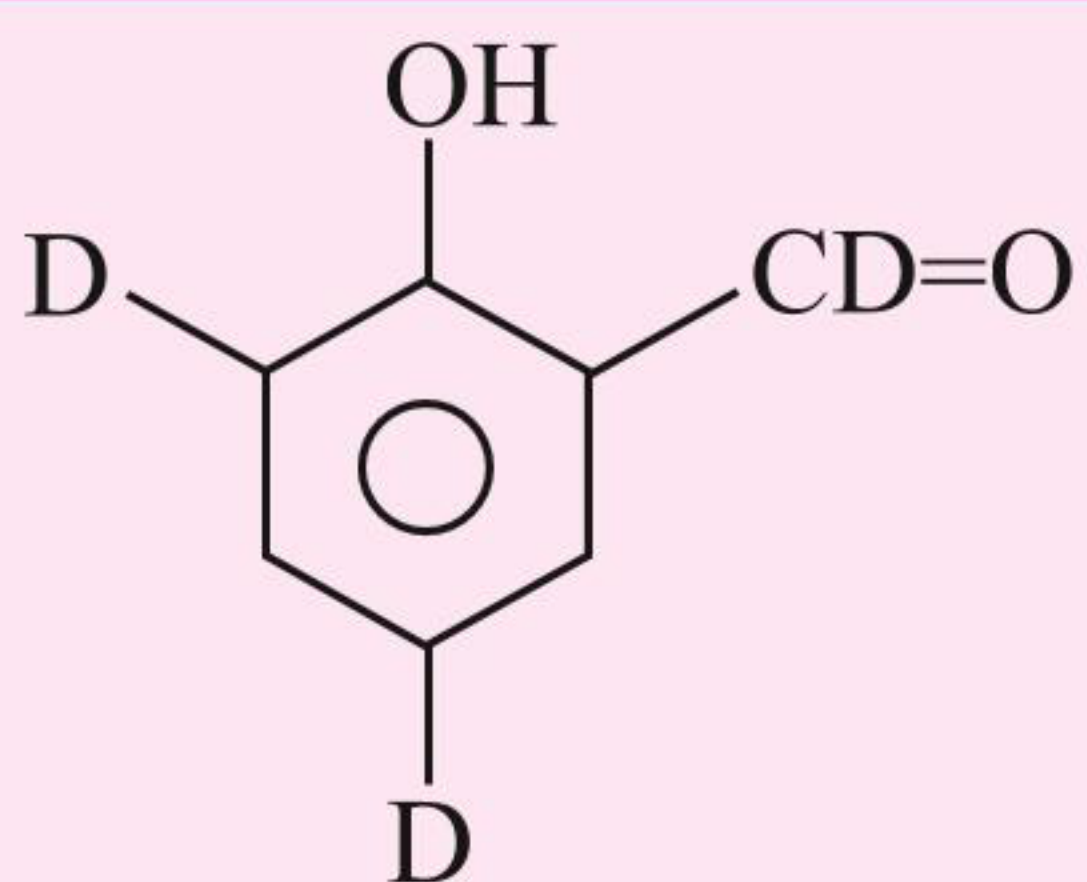
3.	Column I		Column II
	Reaction		Mechanism
a.		p.	Ring expansion
b.		q.	Ring contraction
c.		r.	Carbocation
d.		s.	Rearrangement
		t.	Radical anion

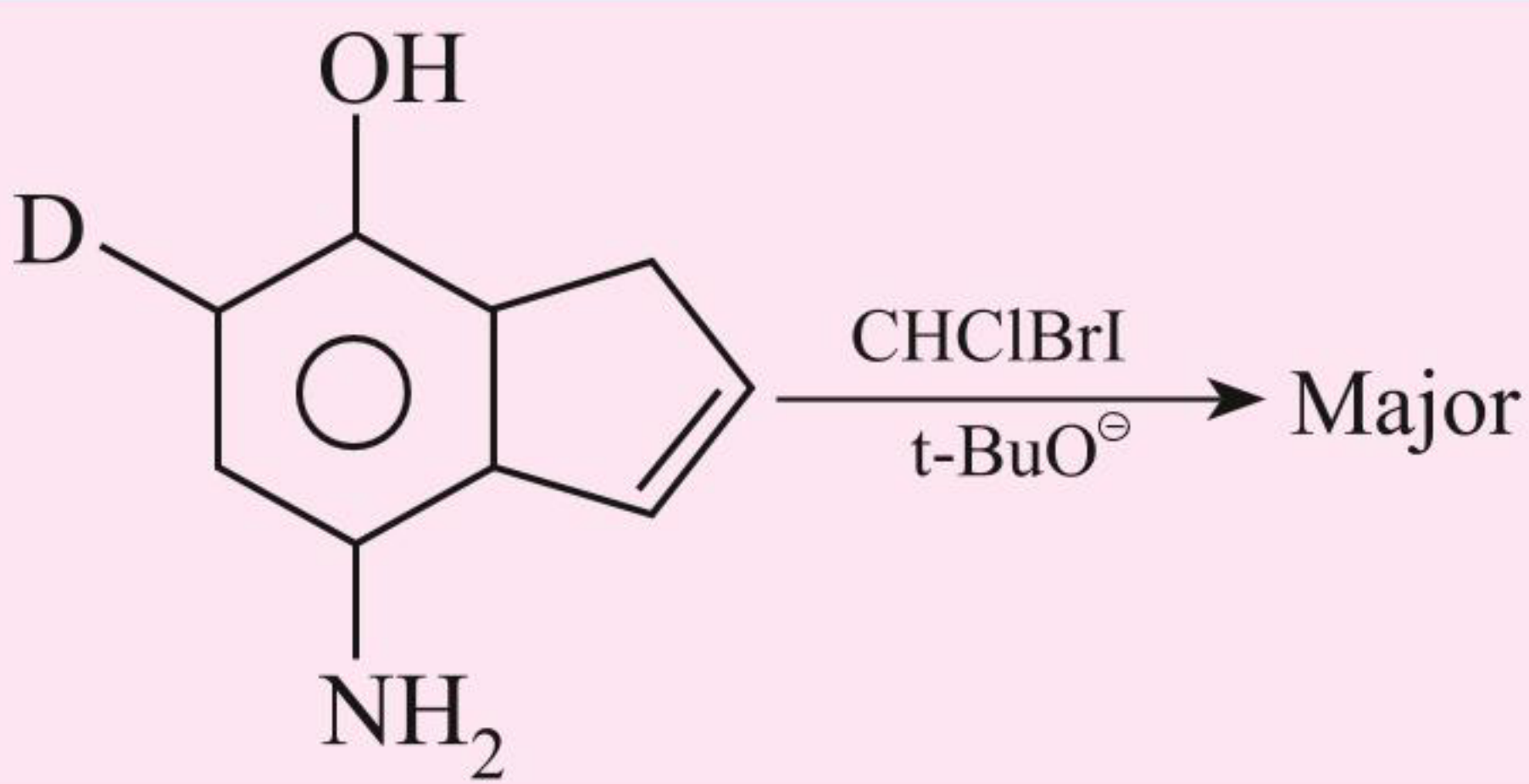
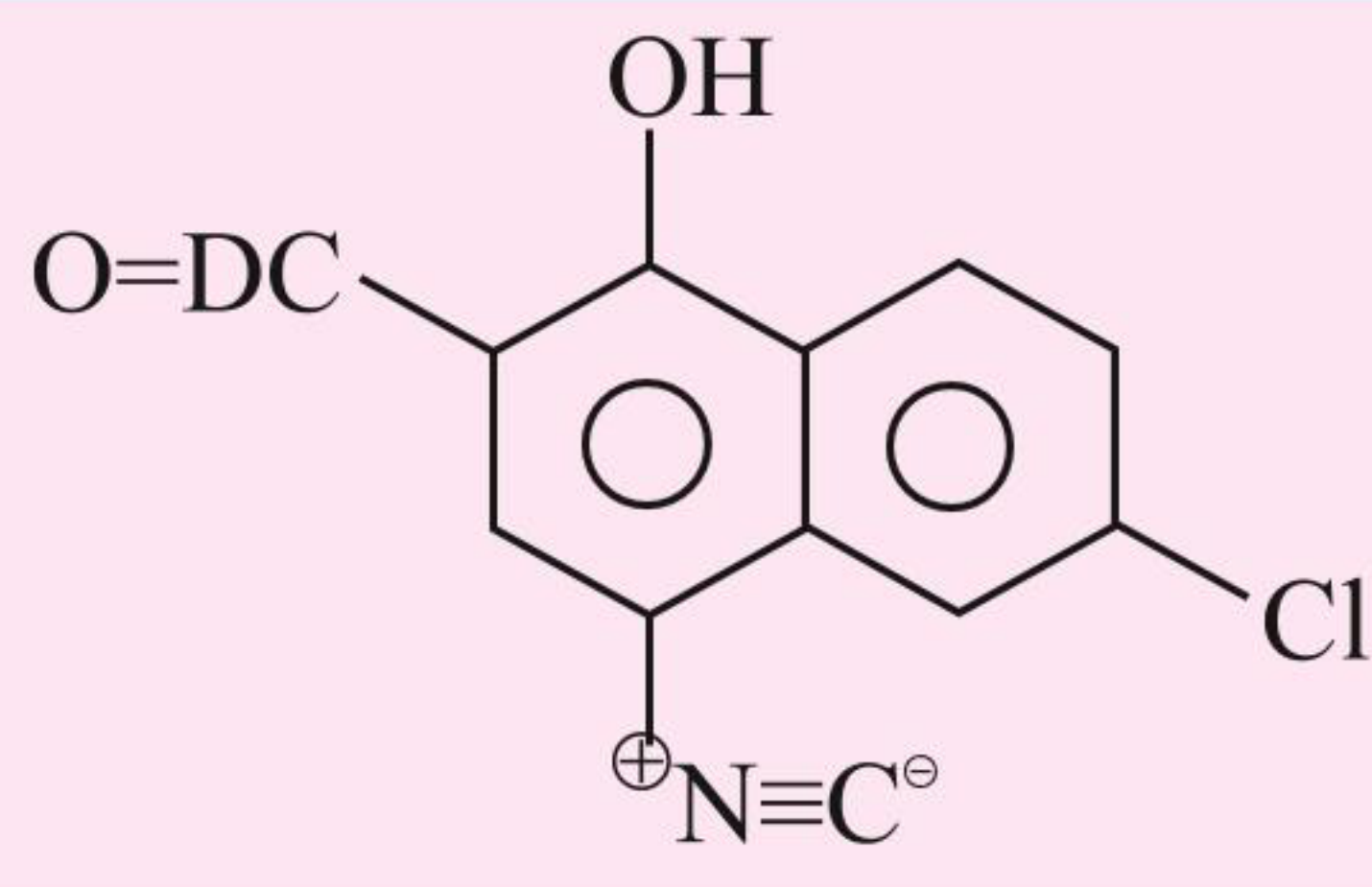
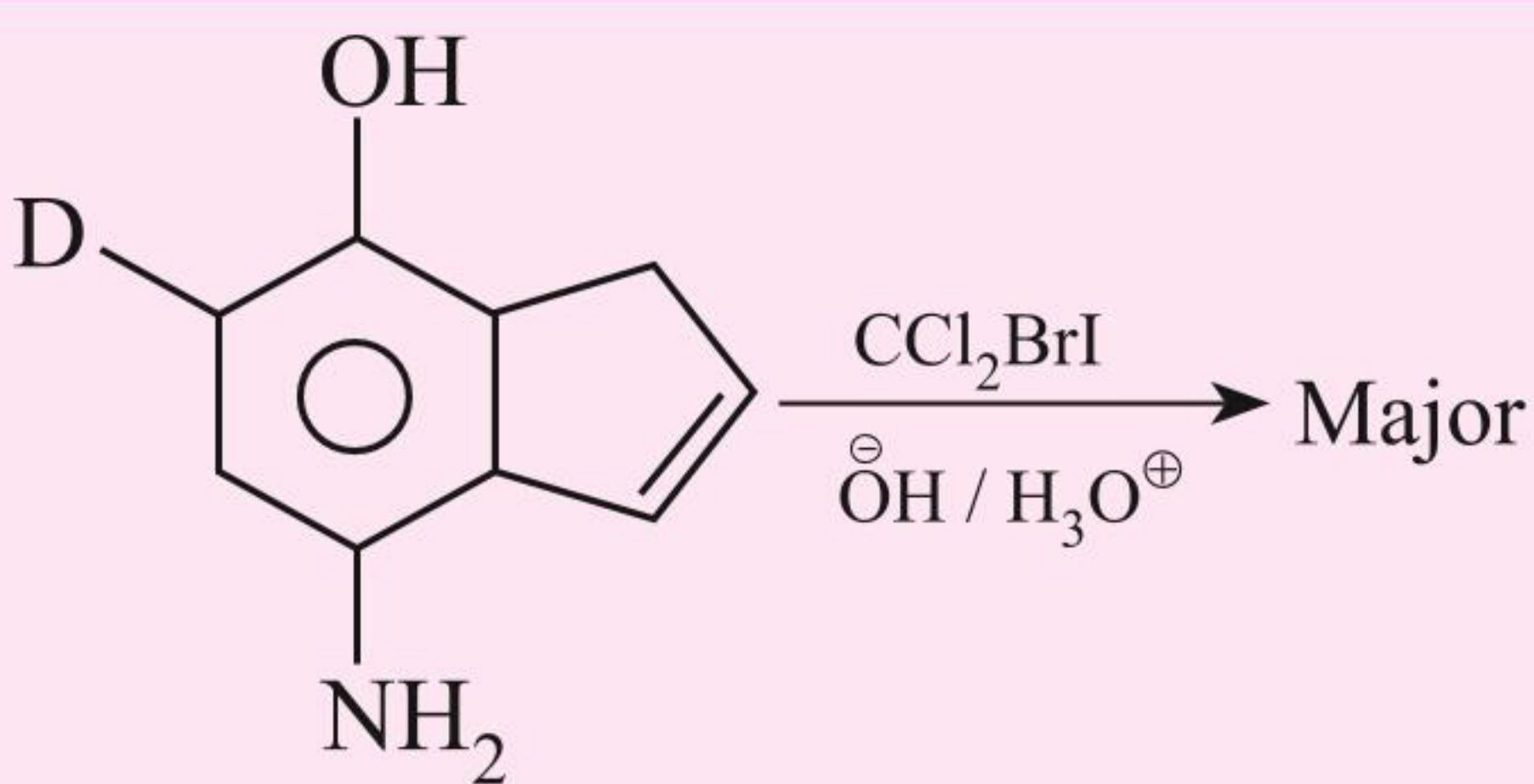
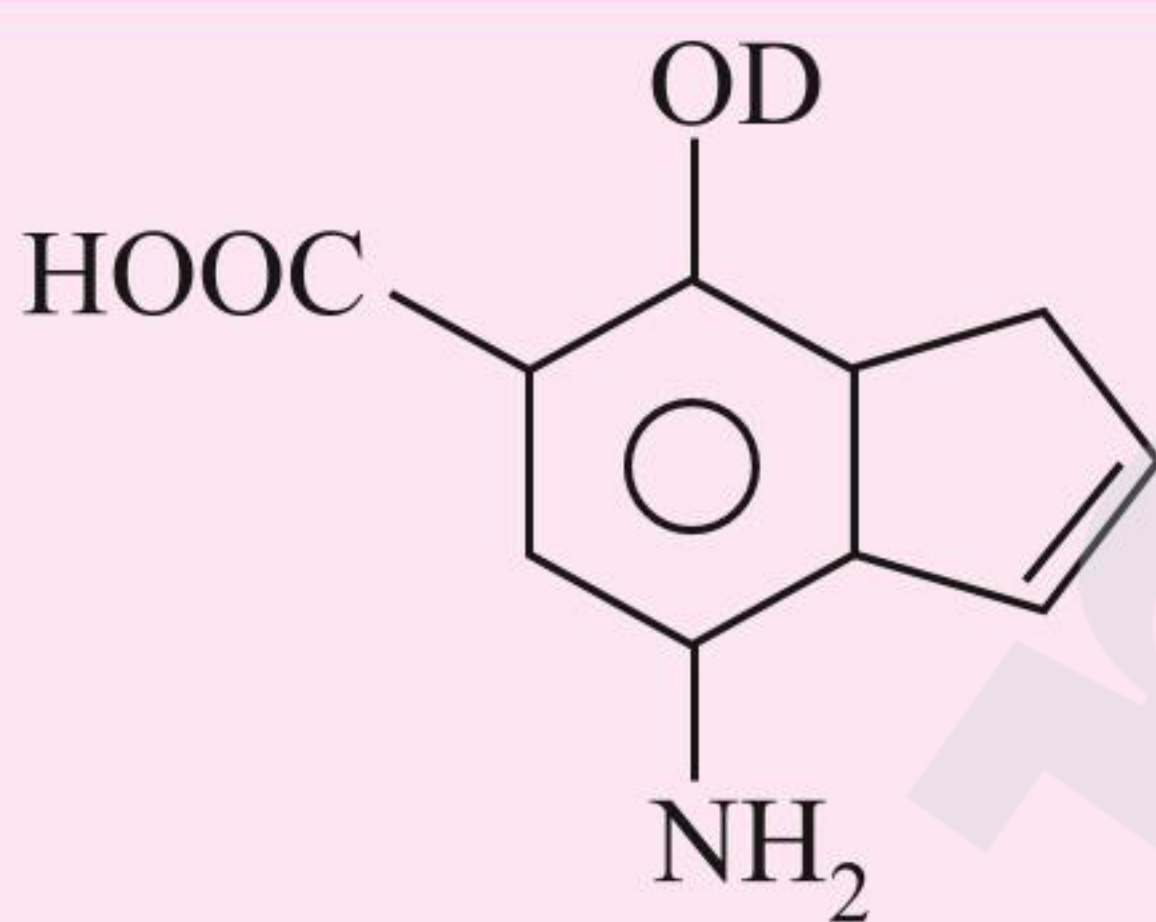
4.	Column I		Column II
	Reaction		Mechanism
a.		p.	Vinylic radical
b.		q.	Radical anion
c.		r.	<i>trans</i> -Vinylic anion
d.		s.	Concerted mechanism

5.	Column I		Column II
	Reaction		Stereochemistry
a.	 (I)	p.	Overall syn addition
b.	(I) $\xrightarrow[\text{H}_3\text{O}^+]{\text{MCPBA}}$	q.	Optically inactive due to external compensation.
c.	(I) $\xrightarrow{\text{Br}_2/\text{H}_2\text{O}}$	r.	Optically inactive due to internal compensation.
d.	(I) $\xrightarrow[\text{KMnO}_4]{\text{Cold alk.}}$	s.	Product has two chiral centres.
		t.	Diastereomers will be formed.

6.	Column I		Column II
	Reaction		Products
a.	 (I)	p.	MeCH ₂ Me
b.	(I) $\xrightarrow[\text{2. CH}_3\text{COOH}]{\text{1. B}_2\text{H}_6 + \text{THF}}$ (III)	q.	
c.	(I) $\xrightarrow[\text{2. AgNO}_3 + \text{NaOH}]{\text{1. B}_2\text{H}_6 + \text{THF}}$ (IV)	r.	
d.	 (P)	s.	
e.	(P) $\xrightarrow[\text{2. AgNO}_3 + \text{NaOH}]{\text{1. B}_2\text{H}_6 + \text{THF}}$ R	t.	 (I)
f.	(P) $\xrightarrow[\text{2. H}_2\text{O}_2 + \text{OH}^-]{\text{1. B}_2\text{H}_6 + \text{THF}}$ S	u.	

7. Match the items given in column I with that in column II and III.

	Column I		Column II		Column III
	Reactions		Products		Characteristics
a		i		p	:CCl Br carbene
b		ii		q	Reimer-Tiemann reaction

c		iii		r	Kolbe's reaction
d		iv		s	Carbyl-amine reaction

For Q.8 to Q.11: Answer the question given below by appropriately matching the information given in three column of the following table

	Reactant		Reagent		Characteristics
a	Cumene	i	Mg/Hg, Δ , H_3O^+	p	Addition and elimination
b	Benzene	ii	$2\text{Cl}_2 + \text{FeCl}_3$	q	1, 2 – H^\ominus shift
c	Phenol	iii	$3\text{Cl}_2 + \text{FeCl}_3, \text{OH}^\ominus$	r	Susceptible to oxidation
d	Acetophenone	iv	$\text{O}_2, \text{H}_3\text{O}^+$	s	Radical anion
e	Acetone				

8. For the synthesis of acetone (by product), the correct combination is:

- (1) a—iv—p (2) a—iv—q
(3) b—iv—q (4) c—iv—p

9. For the synthesis of 2, 4-Dichloro phenol, the correct combination is:

- (1) b—iii—p (2) b—ii—p
(3) c—ii—r (4) c—ii—p

10. For the synthesis of 2, 4-Dichloro phenol, the incorrect combination is:

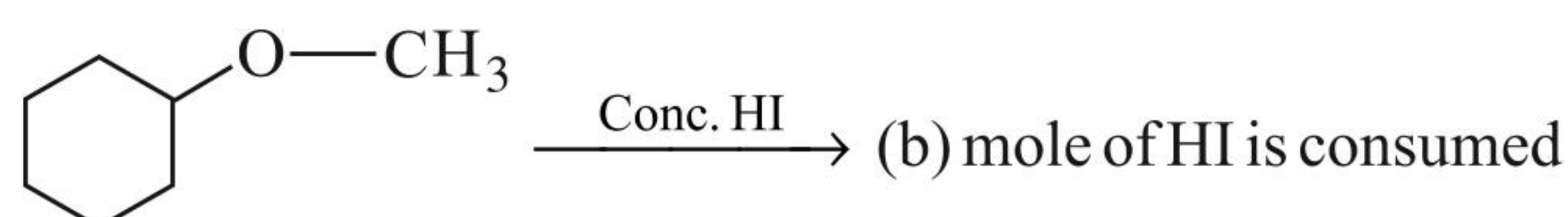
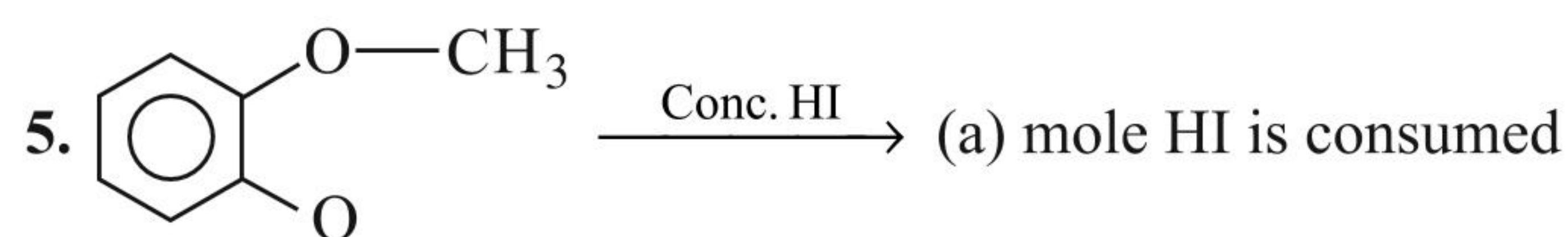
- (1) b—iii—p (2) c—ii—q
(3) c—ii—r (4) c—iii—r

11. For the synthesis of pinacol with 3 isomers the correct combination is:

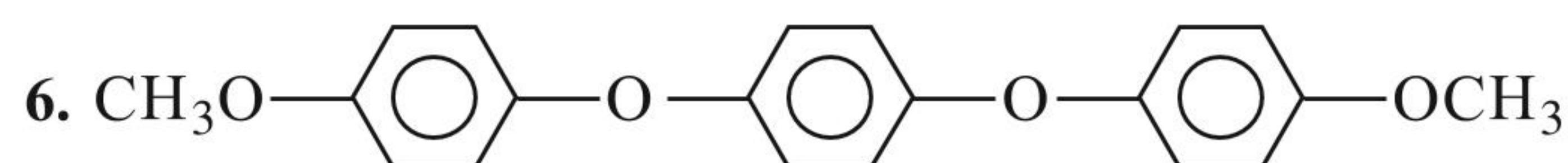
- (1) e—i—s (2) e—i—q
(3) d—i—q (4) d—i—s

gm of AgI. If the molecular weight of compound (A) is 134, the number of ($-\text{OCH}_3$) group(s) in the compound (A) is:

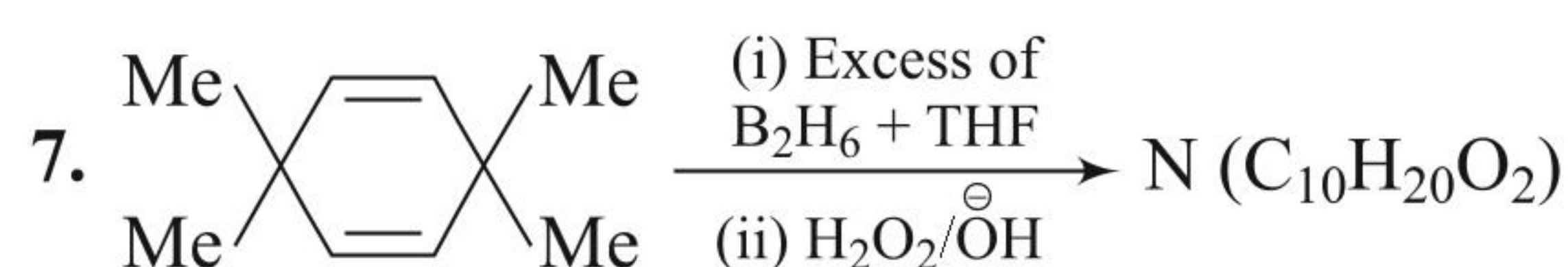
4. If (dl) or (\pm) 2-methyl butanoic acid were esterified by reaction with (dl) or (\pm) 2-butanol, how many optically active compounds would be present in the final equilibrium reaction mixture?



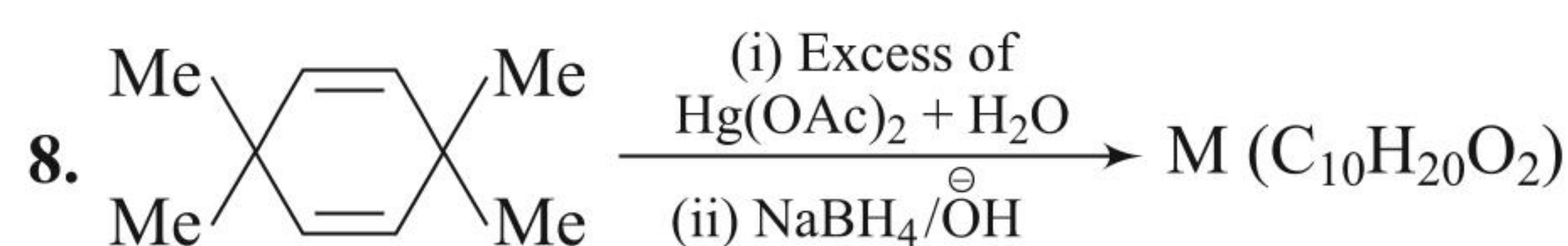
Sum of $a + b =$



How many moles of HI consumed in above reaction?



Give the numerical value of N (total number of isomers including stereoisomers)



Give the numerical value of M (total number of isomers including stereoisomers)

Numerical Value Type

- How many isomeric alcohols (including stereo isomers if any) are possible for the compound with molecular formula $\text{C}_5\text{H}_{12}\text{O}$
- How many cyclic (including stereo isomers) alcohols are possible for the compound with molecular formula $\text{C}_4\text{H}_7\text{OH}$
- In Zeisel's method for the determination of methoxyl groups, a sample of 2.68 gm of a compound (A) gave 14.08

Archives

JEE ADVANCED

Single Correct Answer Type

1. In the reaction c1ccccc1OC $\xrightarrow{\text{HBr}}$ the product are:

- (1) BrC1=CC=CC=C1OC and H2 (2) c1ccccc1Br and CH3Br
 (3) c1ccccc1Br and CH3OH (4) c1ccccc1O and CH3Br

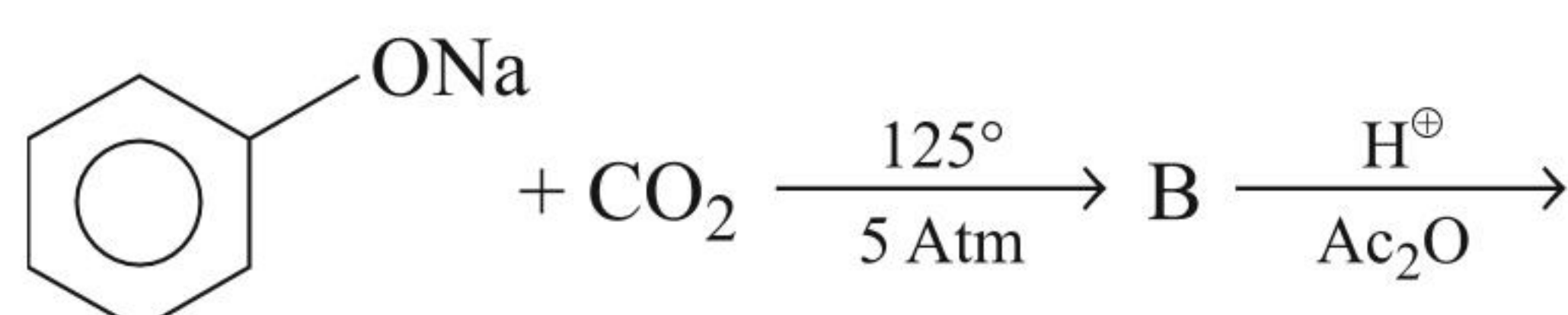
(IIT-JEE 2010)

2. The most suitable reagent for the conversion of R-CH2-OH \rightarrow R-CHO is:

- (1) CrO3
 (2) PCC (Pyridinium Chlorochromate)
 (3) KMnO4
 (4) K2Cr2O7

(JEE Advanced 2014)

3. Sodium phenoxide when heated with CO2 under pressure at 125°C yields a product which on acetylation produces C.

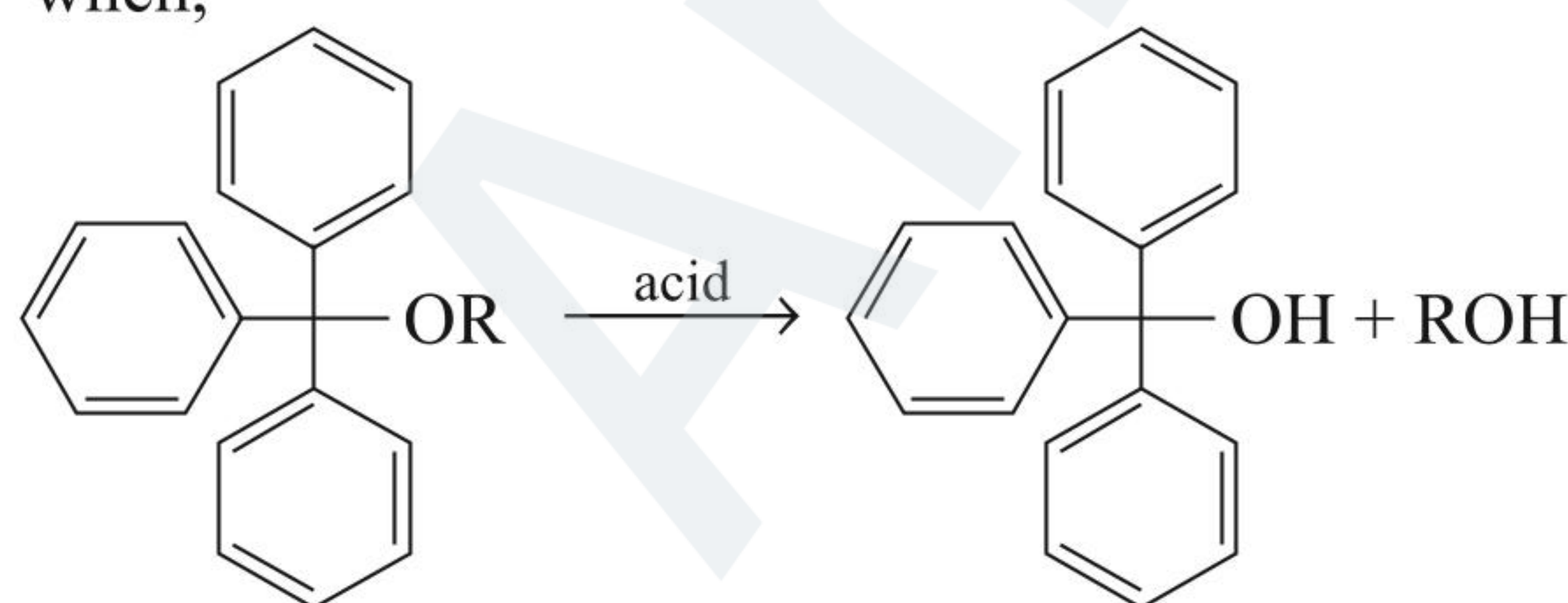


The major product C would be:

- (1) CC(=O)Oc1ccccc1C(=O)O (2) CC(=O)Oc1ccccc1C(=O)O
 (3) CC(=O)Oc1ccccc1C(=O)O (4) CC(=O)Oc1ccccc1C(=O)O

(JEE Advanced 2014)

4. The acidic hydrolysis of ether (X) shown below is fastest when,

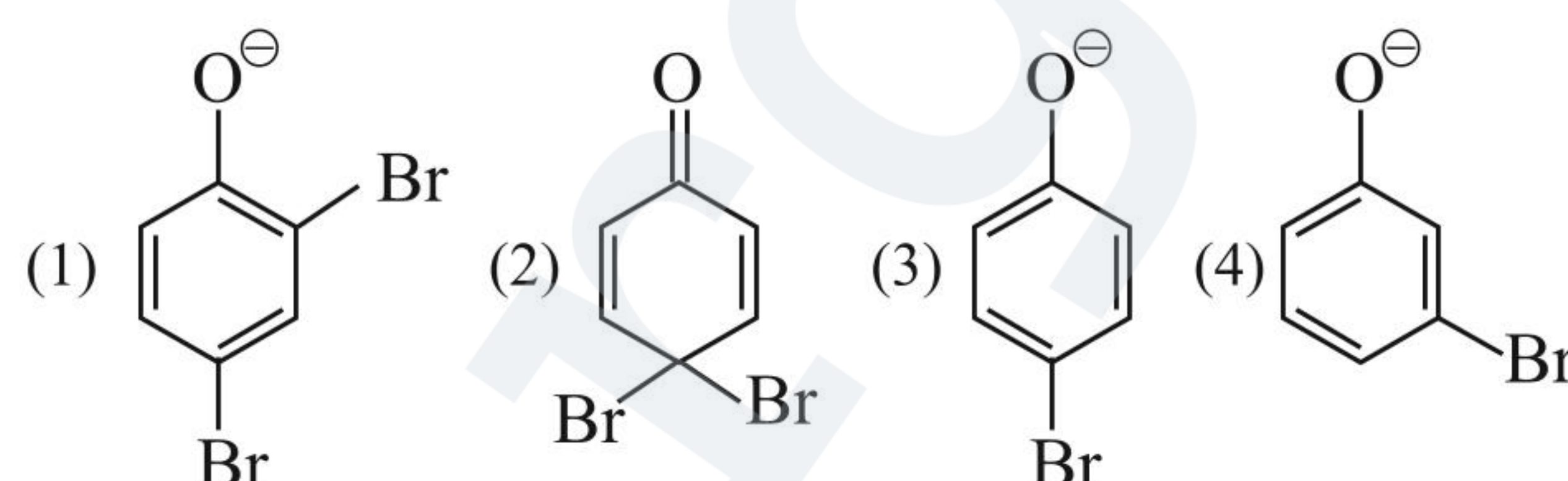


- (1) one phenyl group is replaced by a methyl group.
 (2) one phenyl group is replaced by a para-methoxyphenyl group
 (3) two phenyl groups are replaced by two para-methoxyphenyl groups
 (4) no structural change is made to X

(JEE Advanced 2014)

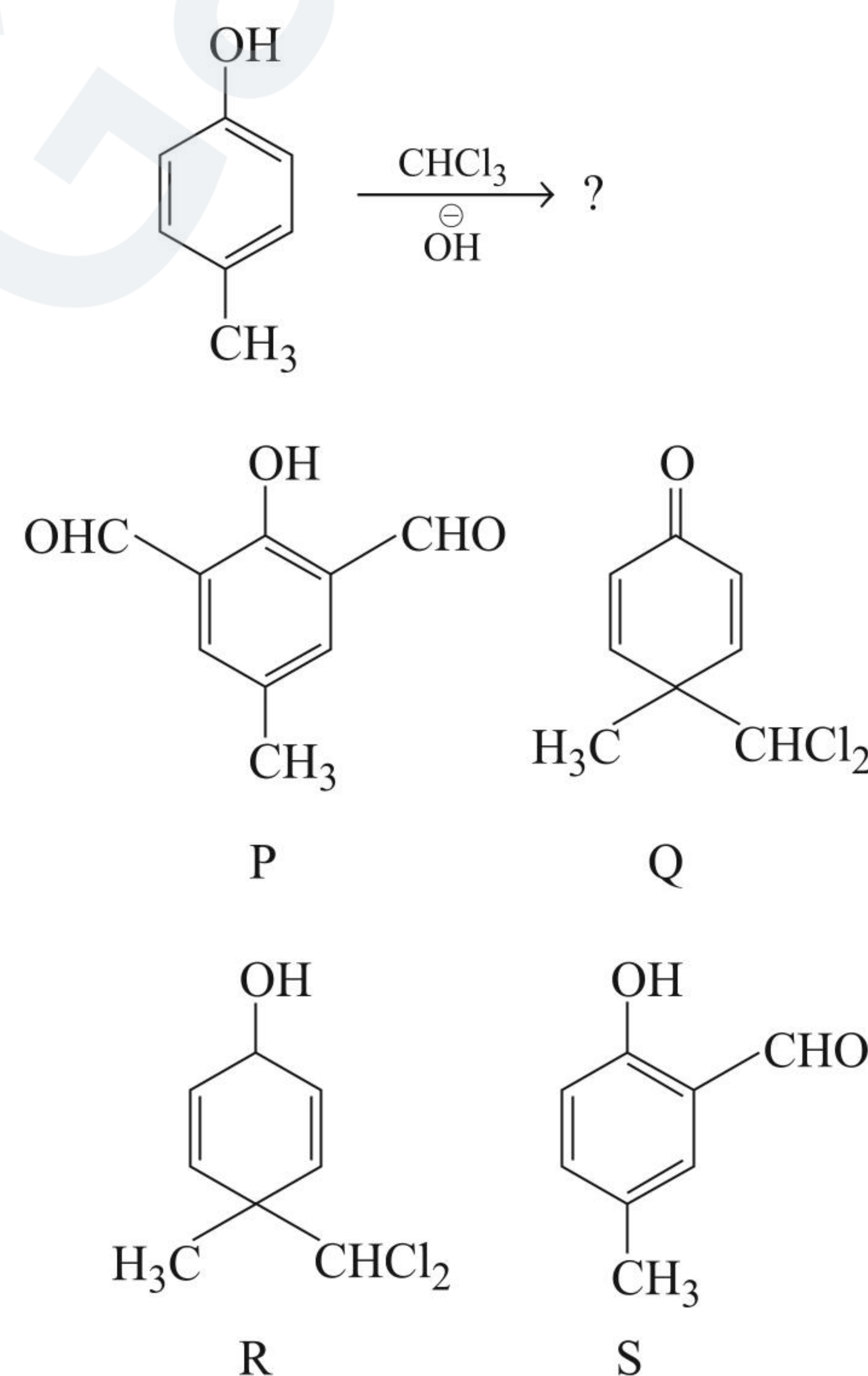
Multiple Correct Answers Type

1. In the reaction c1ccccc1O $\xrightarrow{\text{NaOH(aq.)}/\text{Br}_2}$ the intermediate(s) is/are:



(IIT-JEE 2010)

2. In the following reaction, the product(s) formed is(are)



- (1) P(major) (2) Q(minor)
 (3) R(minor) (4) S(major)

(JEE Advanced 2013)

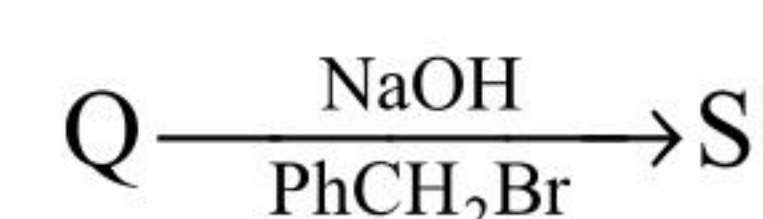
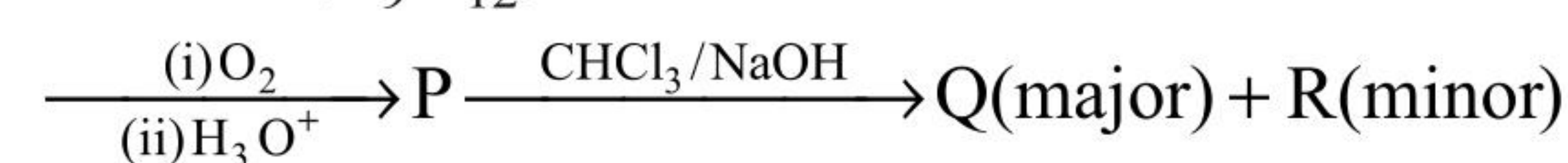
3. The correct combination of names for isomeric alcohols with molecular formula C4H10O is/are

- (1) *tert*-butanol and 2-methylpropan-2-ol
 (2) *tert*-butanol and 1, 1-dimethylethan-1-ol
 (3) *n*-butanol and butan-1-ol
 (4) isobutyl alcohol and 2-methylpropan-1-ol

(JEE Advanced 2014)

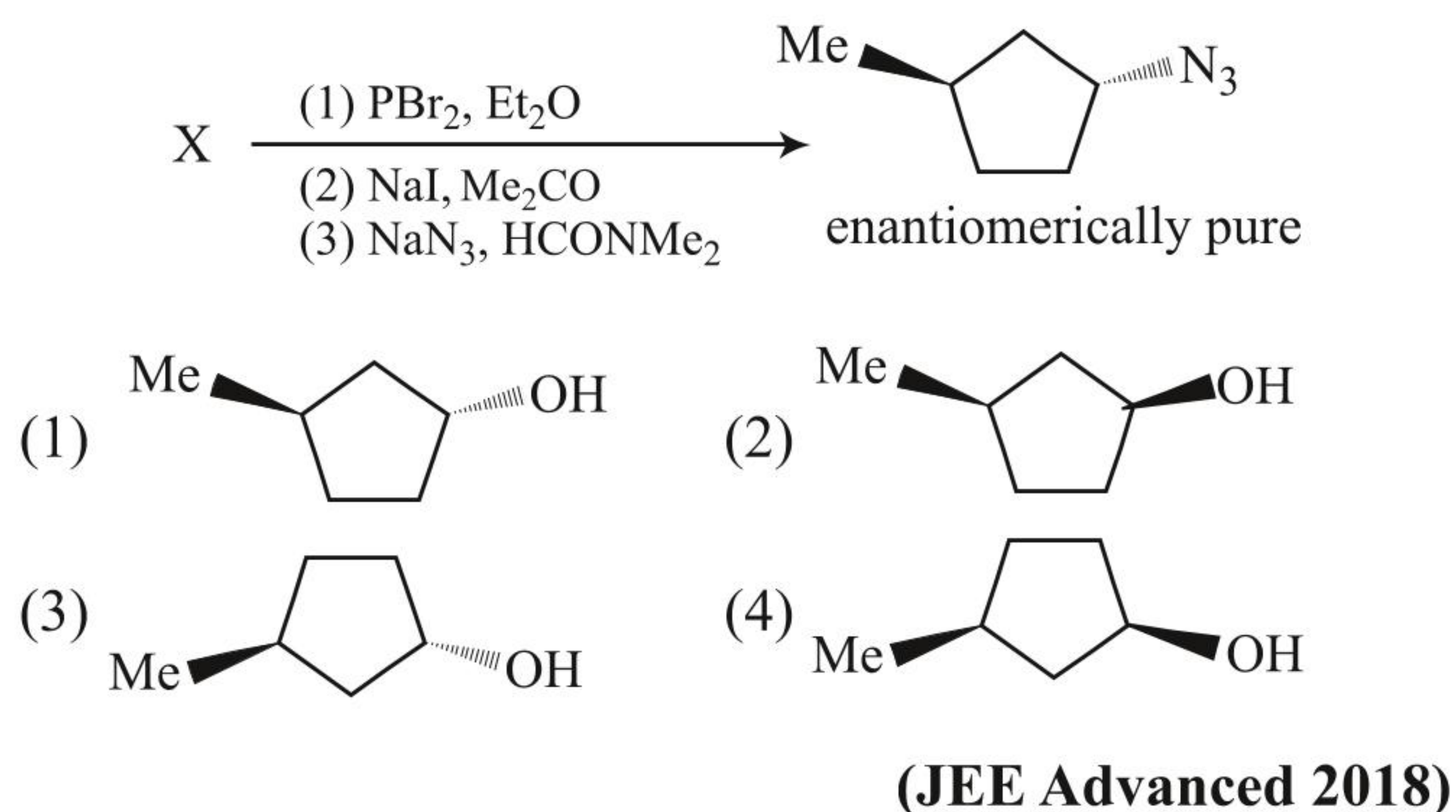
4. The correct statement(s) about the following reaction sequence is(are)

Cumene (C9H12)

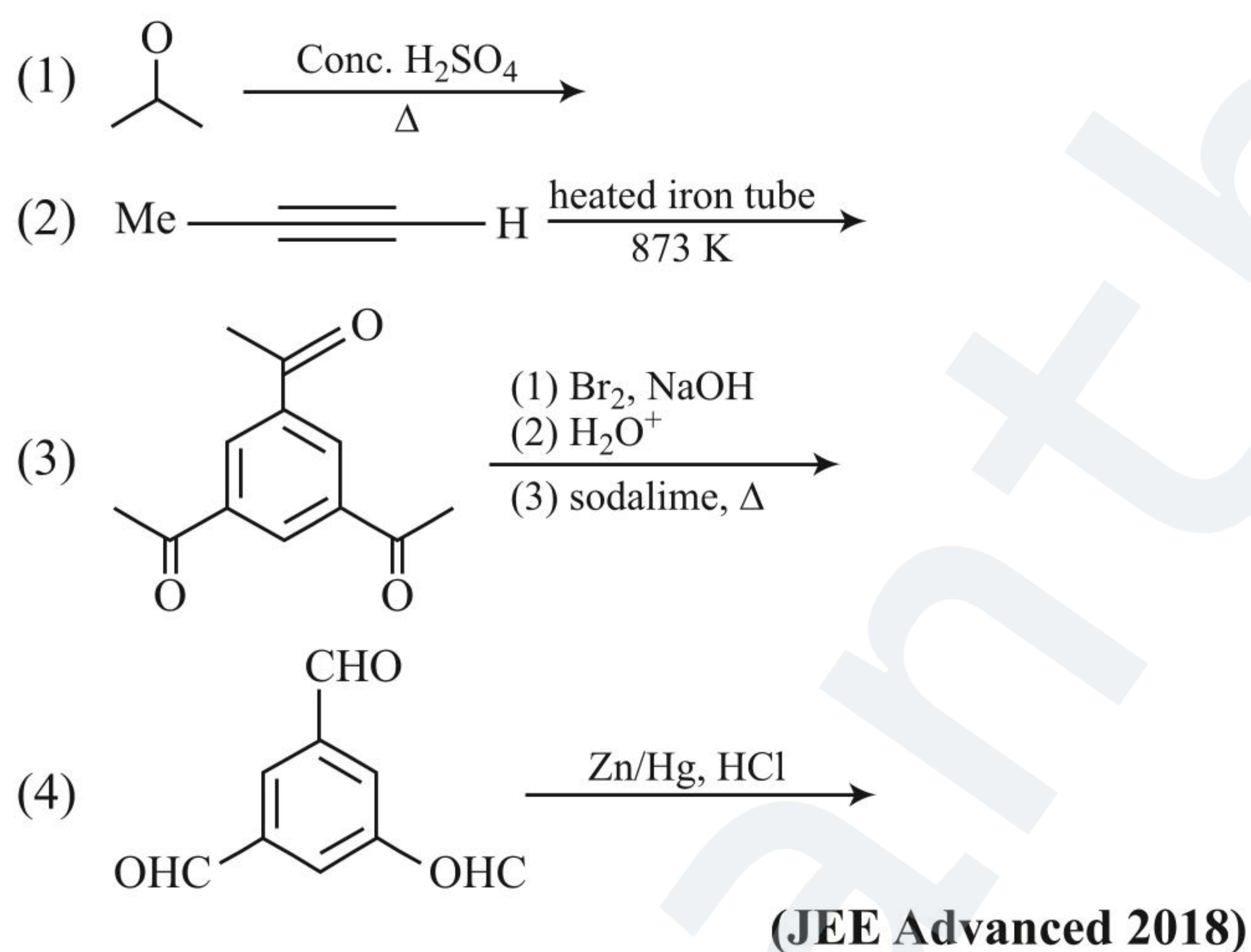


- (1) R is steam volatile
 (2) Q gives dark violet colouration with 1% aqueous FeCl_3 solution
 (3) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
 (4) S gives dark violet colouration with 1% aqueous FeCl_3 solution
(JEE Advanced 2016)

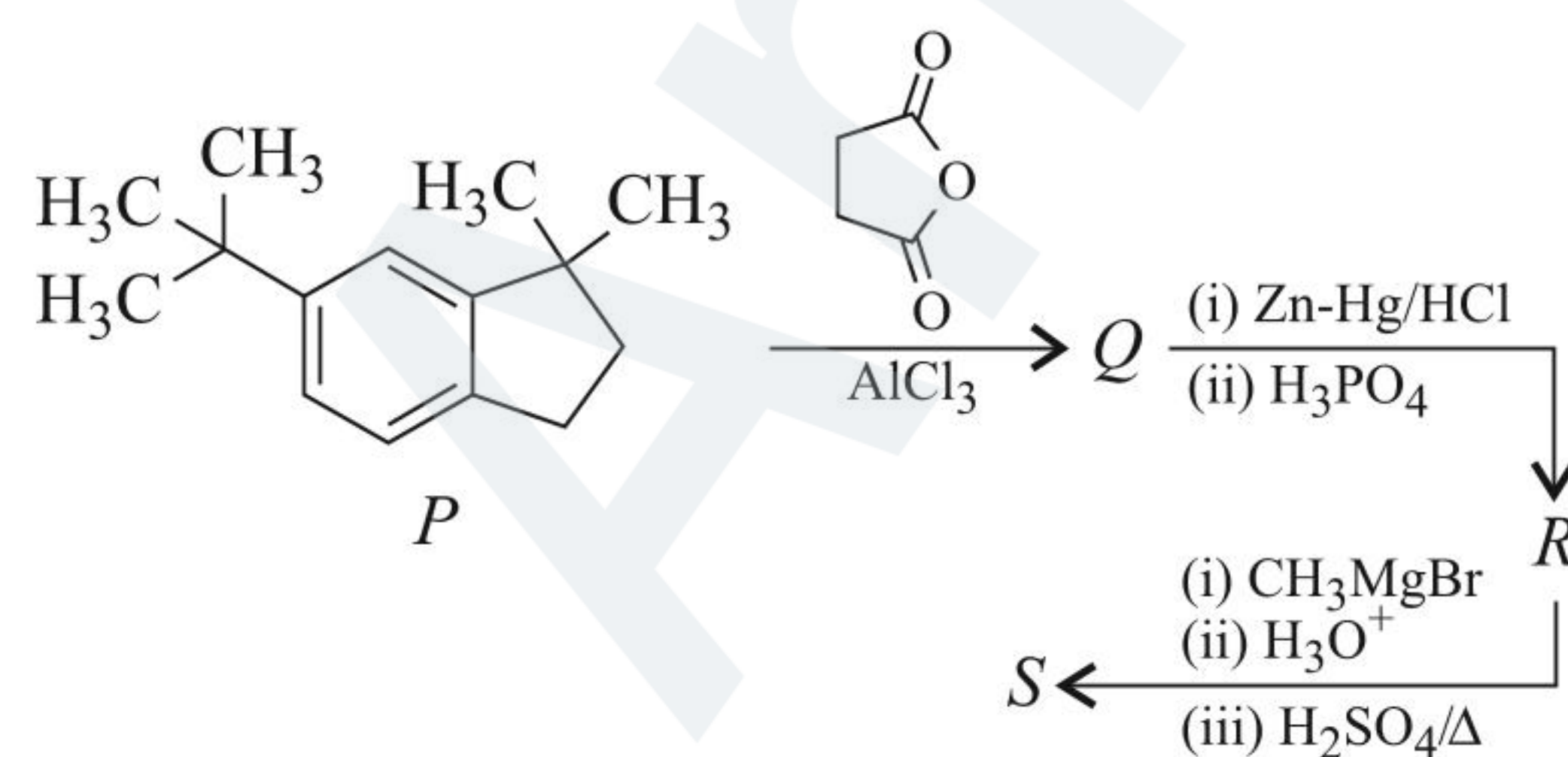
5. In the following reaction sequence, the correct structure(s) of X is (are)



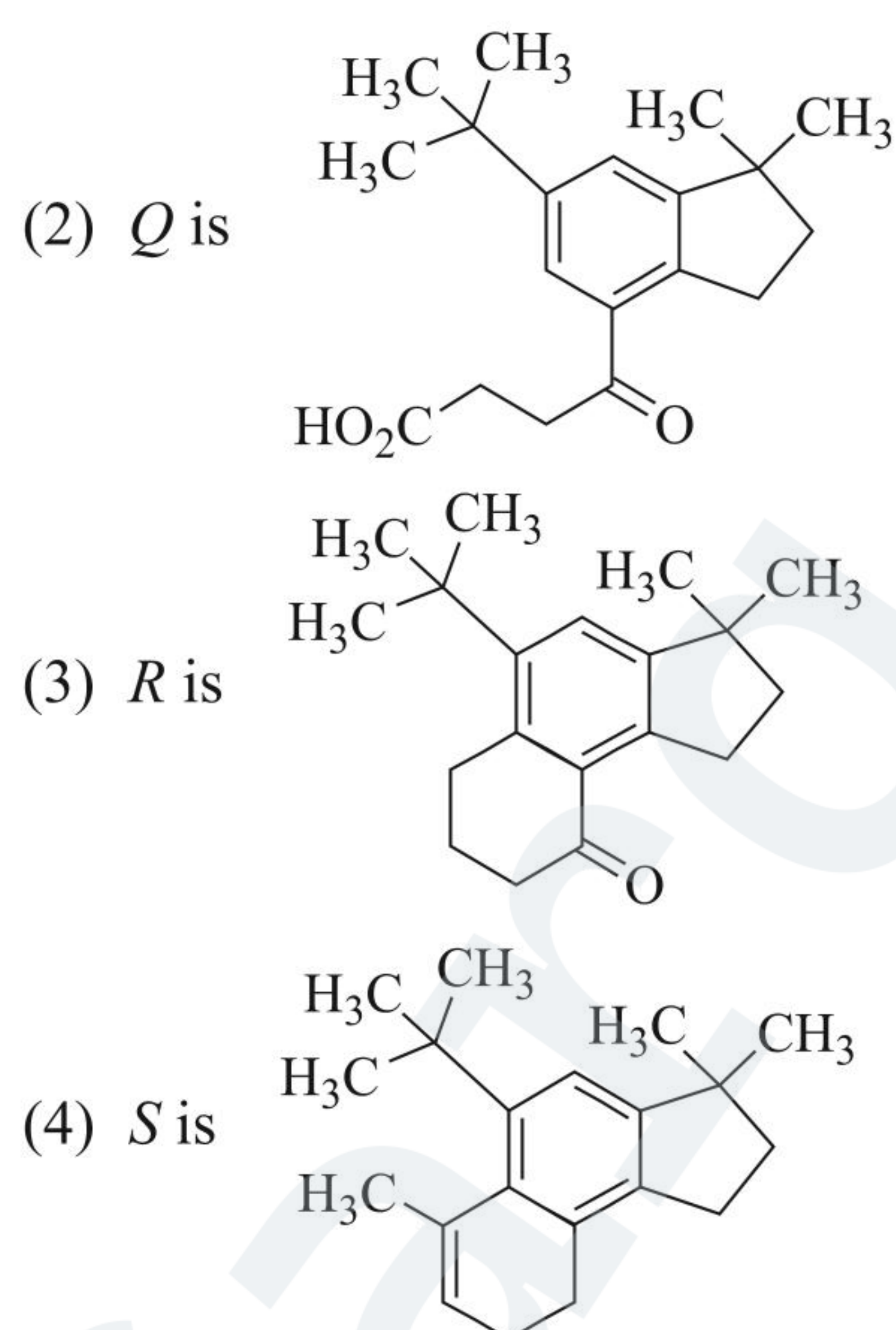
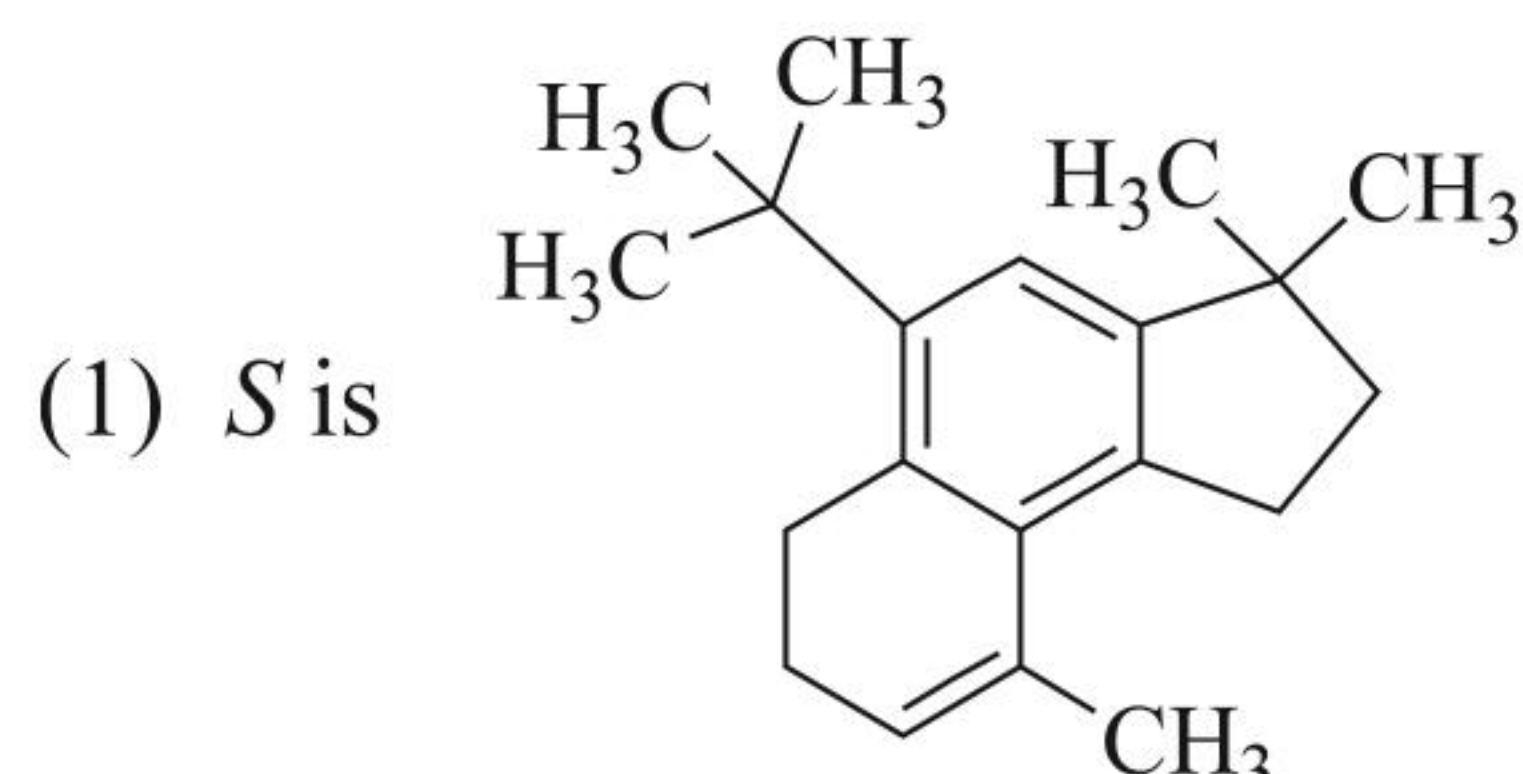
6. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)



7. In the reaction scheme shown below Q, R and S are the major products.



The correct structure of

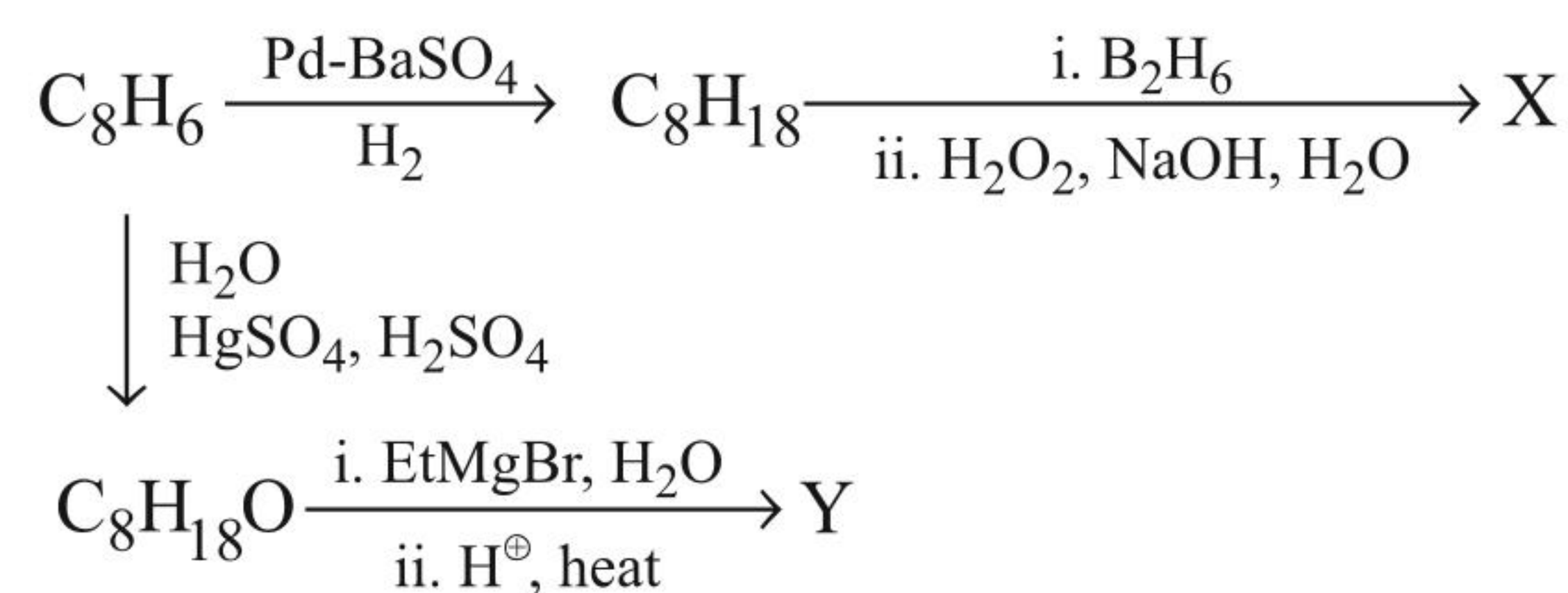


(JEE Advanced 2020)

Linked Comprehension Type

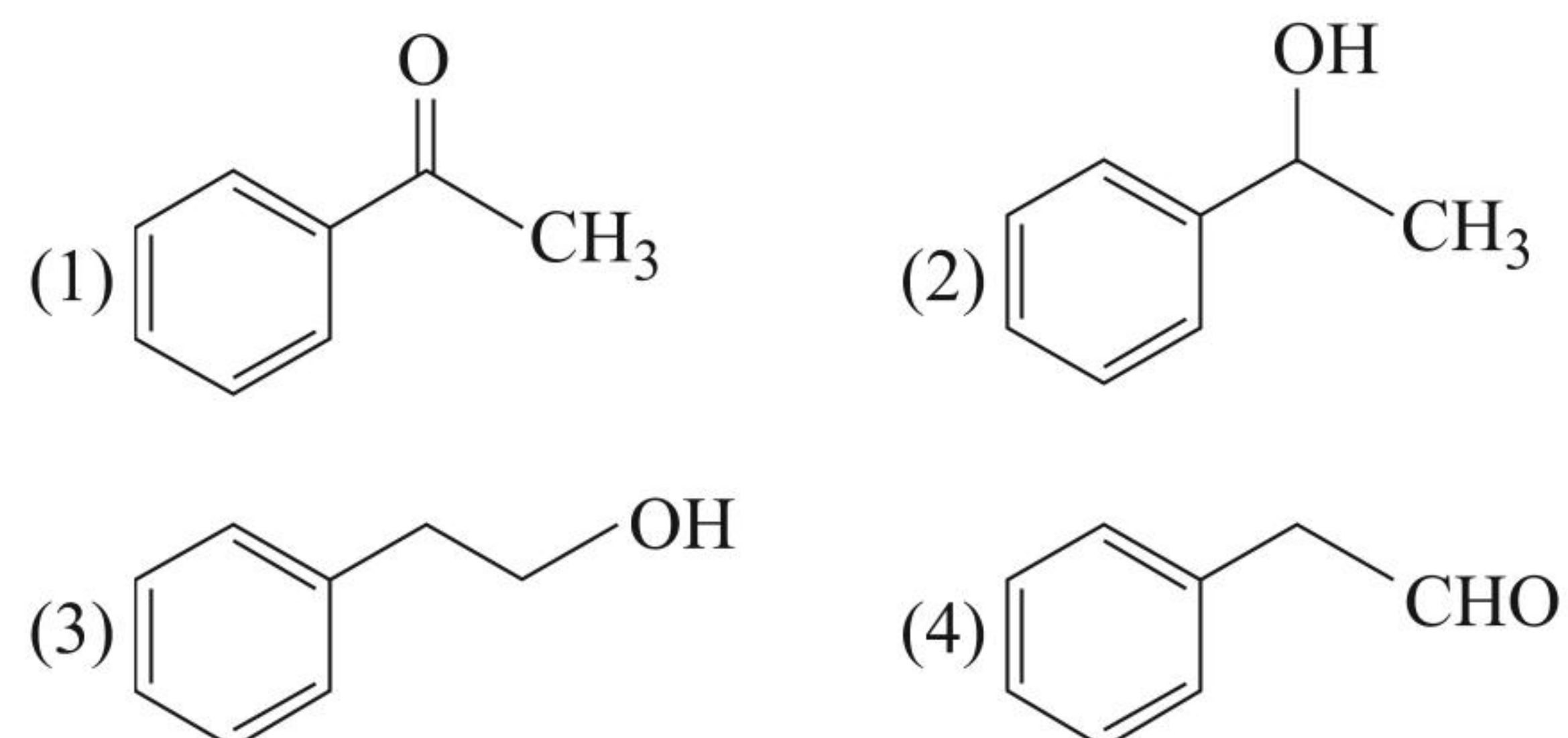
Paragraph 1

In the following reactions

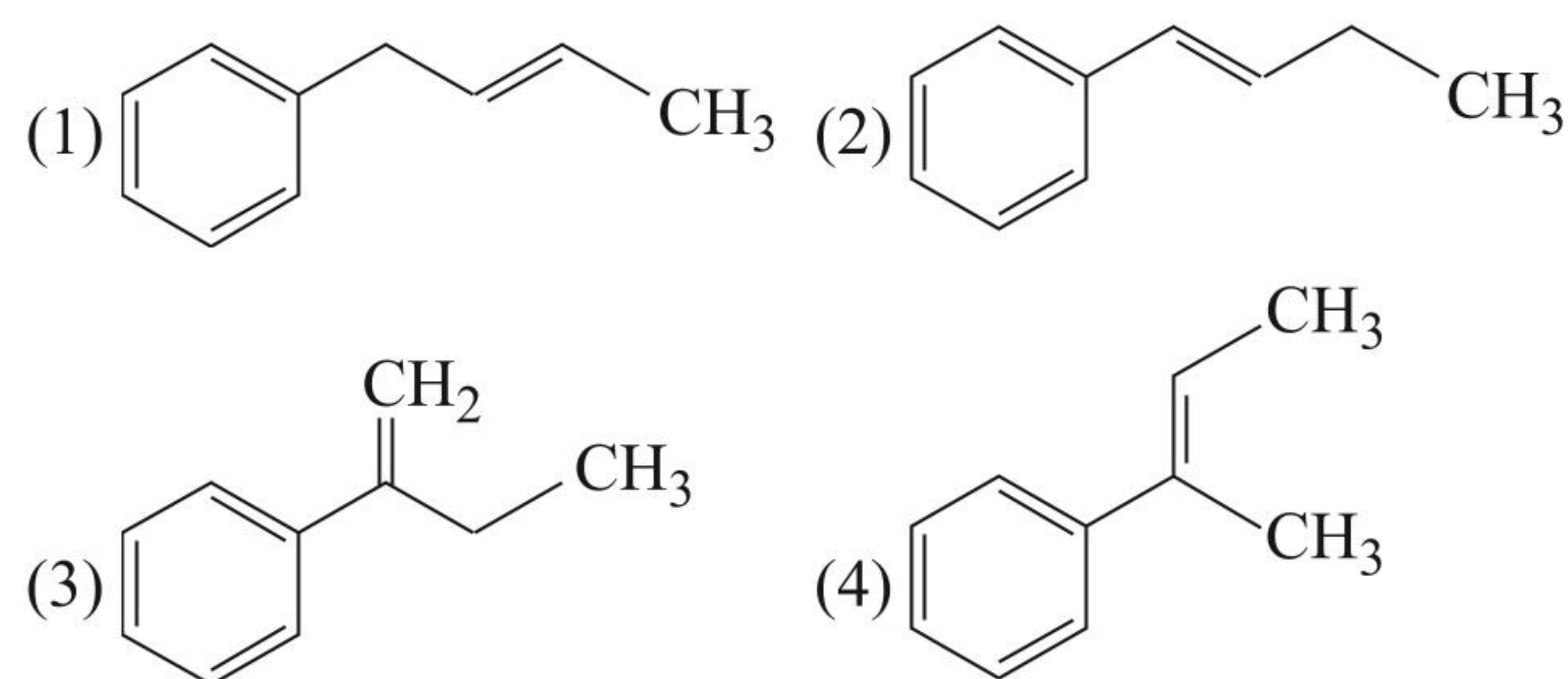


1. Compound X is

(JEE Advanced 2015)



2. The major compound Y is



Numerical Value Type

1. An organic compound ($\text{C}_8\text{H}_{10}\text{O}_2$) rotates plane-polarized light. It produces pink colour with neutral FeCl_3 solution. What is the total number of all the possible isomers for this compound?
(JEE Advanced 2020)

Answers Key

EXERCISES

1. (2) 2. (3) 3. (1) 4. (3) 5. (1)
6. (3) 7. (3) 8. (2) 9. (4) 10. (3)
11. (2) 12. (4) 13. (4) 14. (4) 15. (4)
16. (2) 17. (1) 18. (2) 19. (2) 20. (2)
21. (1) 22. (1) 23. (1) 24. (3) 25. (3)
26. (1) 27. (2) 28. (2) 29. (2) 30. (1)
31. (1) 32. (2) 33. (3) 34. (2) 35. (2)
36. (2) 37. (4) 38. (3) 39. (4) 40. (4)
41. (4) 42. (1) 43. (1) 44. (2) 45. (1)
46. (3) 47. (2) 48. (1) 49. (1) 50. (4)
51. (2) 52. (2) 53. (2) 54. (1) 55. (2)
56. (2) 57. (1) 58. (3) 59. (3) 60. (3)
61. (2) 62. (3) 63. (2) 64. (4) 65. (4)
66. (3) 67. (3) 68. (1) 69. (4) 70. (2)
71. (3) 72. (2) 73. (3) 74. (1) 75. (3)
76. (3) 77. (2) 78. (2) 79. (4) 80. (4)
81. (1) 82. (1) 83. (3) 84. (4) 85. (3)
86. (2) 87. (3) 88. (2) 89. (2) 90. (3)
91. (2) 92. (4) 93. (2) 94. (1) 95. (1)
96. (1) 97. (3) 98. (3) 99. (2) 100. (4)
101. (3) 102. (2) 103. (1) 104. (2) 105. (3)
106. (2) 107. (3) 108. (1) 109. (3) 110. (2)
111. (1) 112. (4) 113. (4) 114. (3) 115. (1)
116. (3) 117. (2) 118. (2) 119. (4) 120. (1)
121. (3) 122. (3) 123. (3) 124. (1) 125. (1)
126. (3) 127. (4) 128. (4)

Multiple Correct Answers Type

1. (1, 4) 2. (1, 2, 3, 4) 3. (2, 3, 4)
4. (1, 4) 5. (1, 2, 3, 4) 6. (1, 2, 4)
7. (3) 8. (1, 2, 3) 9. (4)
10. (1) 11. (1, 3, 4) 12. (2, 3, 4)
13. (1, 3) 14. (1, 2, 3, 4) 15. (1, 2, 3)
16. (2, 4) 17. (1, 3, 4) 18. (1, 3)
19. (1, 2, 4) 20. (1, 2, 3, 4) 21. (1, 3, 4)
22. (2, 3, 4) 23. (2, 3) 24. (1)
25. (1, 2, 3) 26. (2, 3) 27. (2, 3)
28. (1, 2, 3, 4) 29. (3, 4) 30. (1, 2)
31. (1, 2) 32. (1, 2, 3) 33. (1, 2, 3)
34. (1, 2, 4) 35. (2, 3, 4) 36. (2, 3, 4)
37. (1, 2) 38. (1, 2) 39. (1)
40. (1, 4) 41. (2, 4) 42. (4)

43. (3) 44. (1) 45. (1, 2)
46. (1, 2) 47. (3, 4) 48. (2, 4)
49. (1, 4) 50. (1, 3, 4) 51. (1, 2, 4)

Linked Comprehension Type

1. (2) 2. (1) 3. (3) 4. (1) 5. (3)
6. (3) 7. (1) 8. (1) 9. (1) 10. (2)
11. (4) 12. (4) 13. (3) 14. (4) 15. (4)
16. (3) 17. (3) 18. (1) 19. (1)

Matrix Match Type

S. No.	a	b	c	d	e	f
1.	q	r	p, s	t	u	—
2.	q, r	p, s, t	u	p, t	p, r, s	p, s
3.	q, r, s	p, r, s	s	r, s, t	—	—
4.	q	p, q, r	s	s	—	—
5.	p, r, s	q, s	t	p, r, s	—	—
6.	u	p	q	t	s	r
7.	ii, p, q	i, r	iii, p, q, s	iv, r	—	—

8. (2) 9. (1) 10. (3) 11. (4)

Numerical Value Type

1. (8) 2. (7) 3. (3) 4. (4) 5. (3)
6. (2) 7. (6) 8. (6)

ARCHIVES

JEE Advanced

Single Correct Answer Type

1. (4) 2. (2) 3. (3) 4. (3)

Multiple Correct Answers Type

1. (1, 2, 3) 2. (2, 4) 3. (1, 3, 4)
4. (2, 3) 5. (2) 6. (1, 2, 4)
7. (2, 4)

Linked Comprehension Type

1. (3) 2. (4)

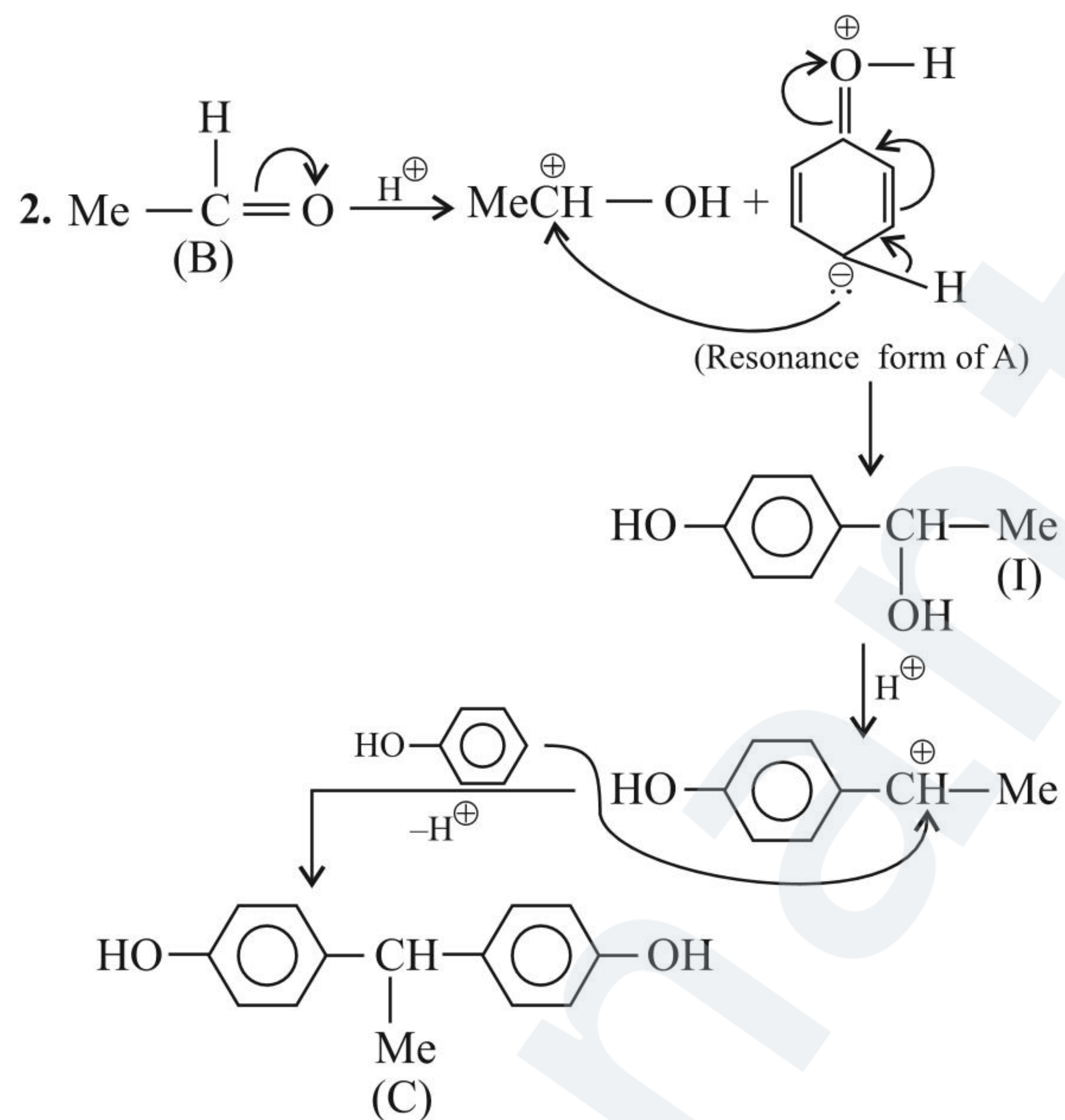
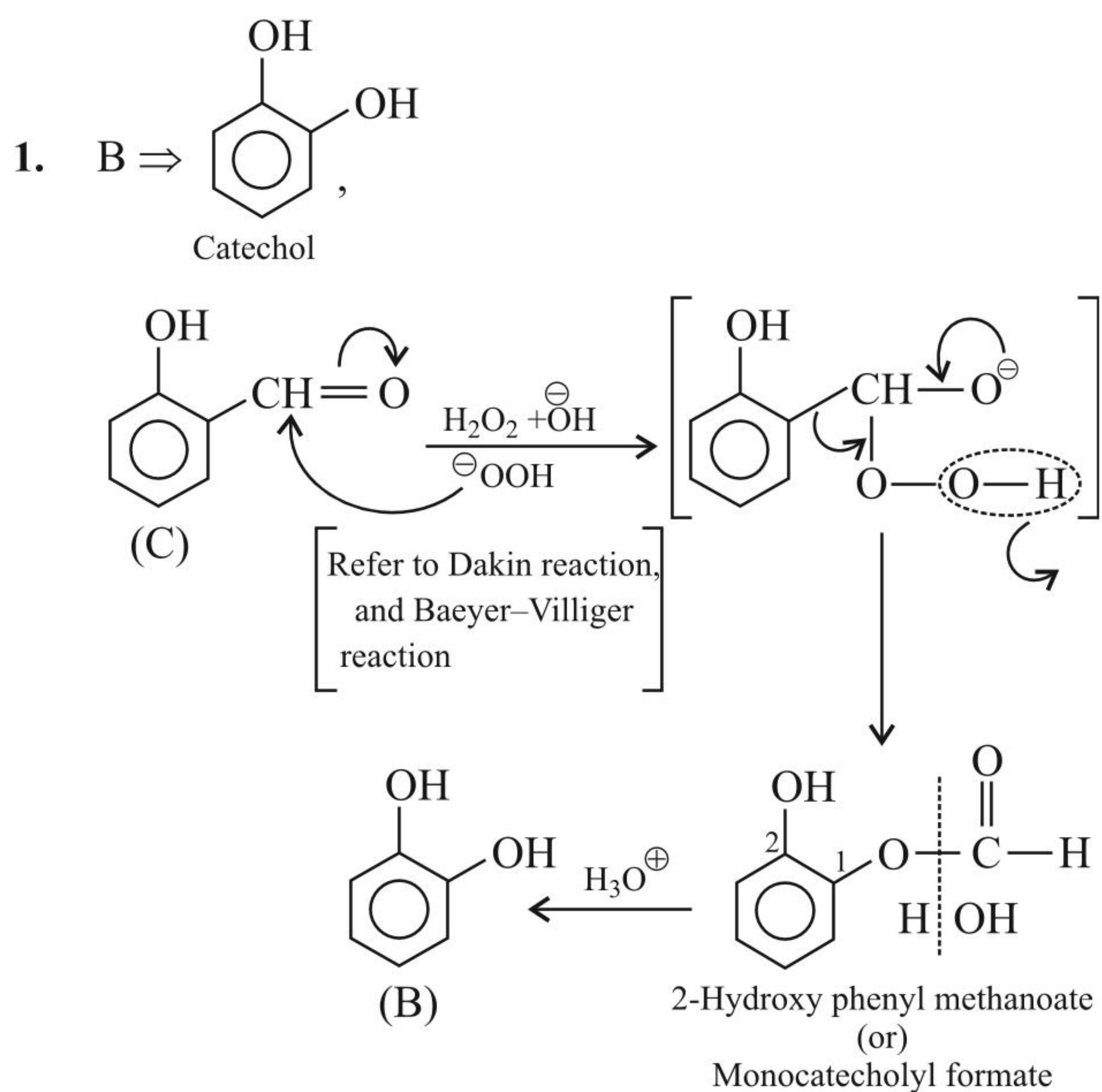
Numerical Value Type

1. (6)

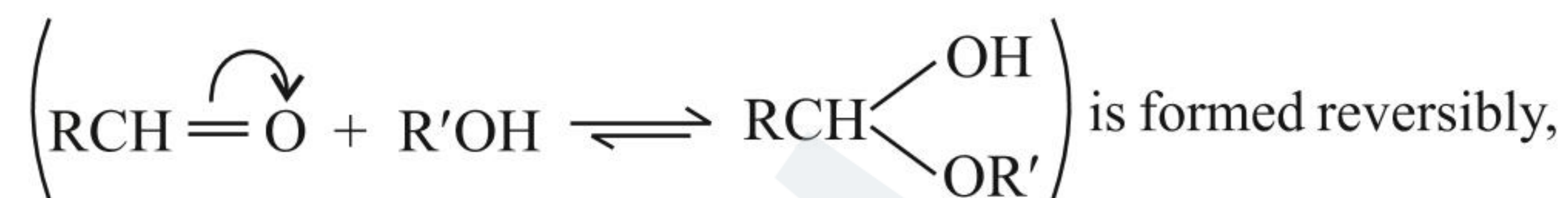
Chapter 4

Concept Application Exercises

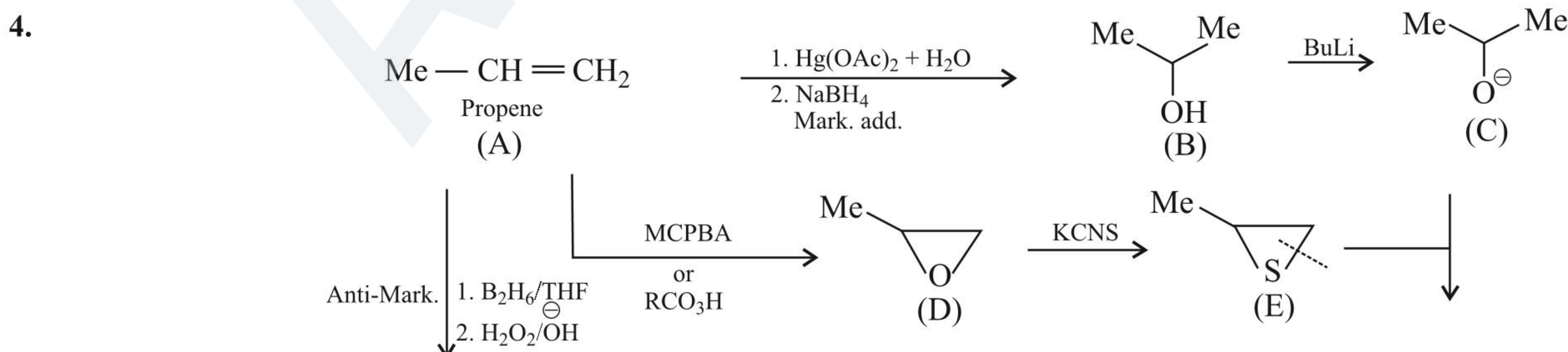
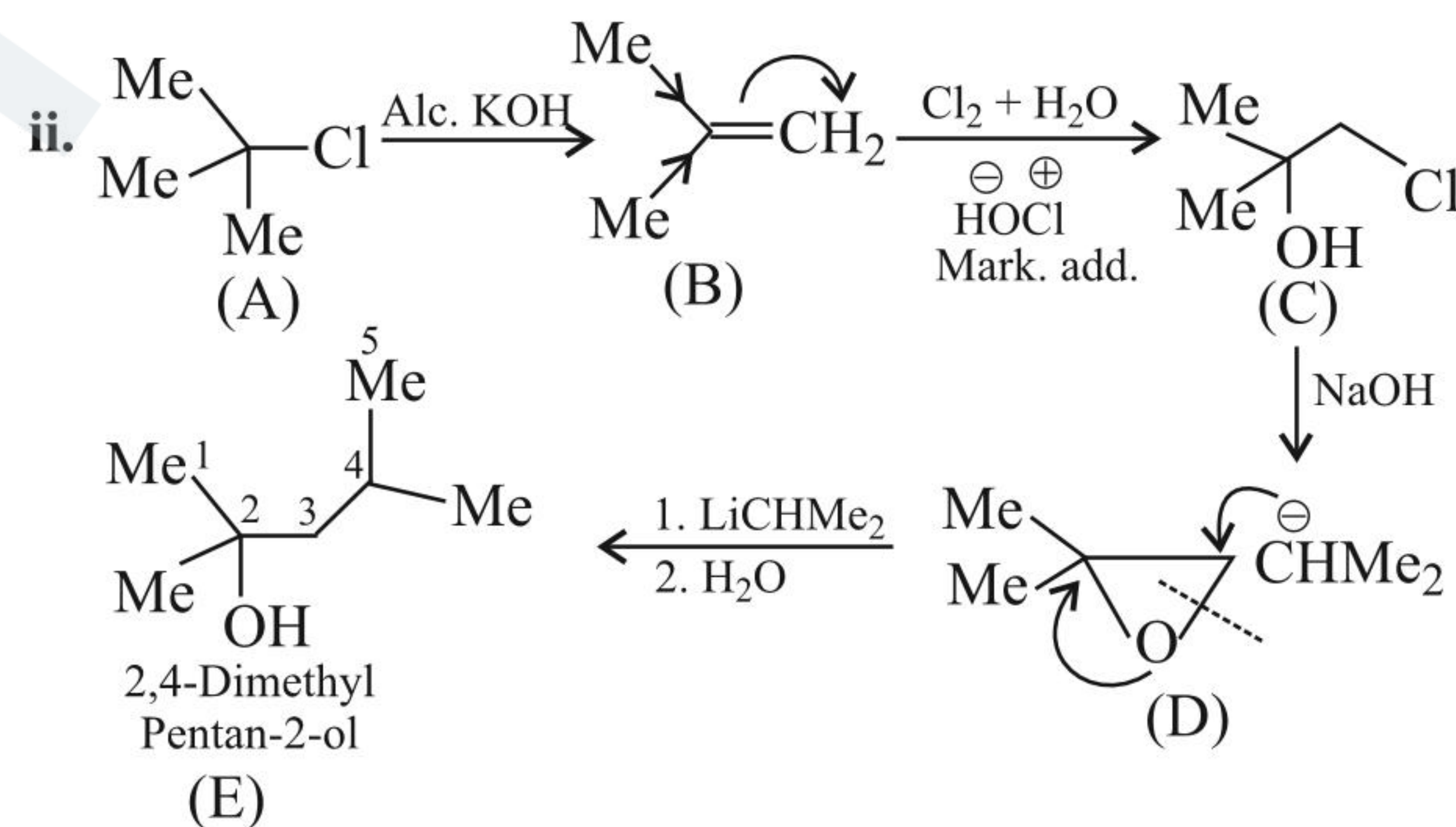
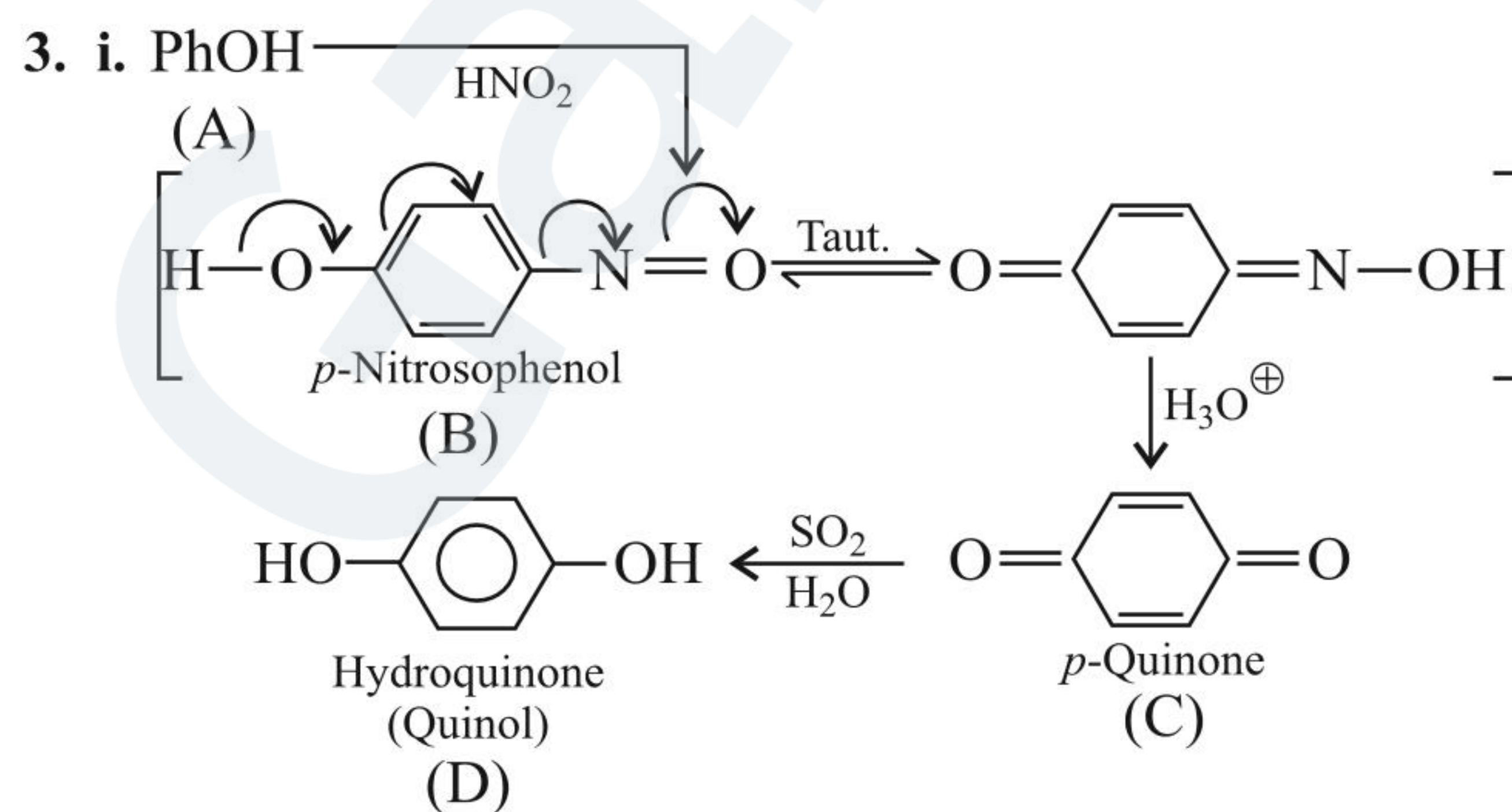
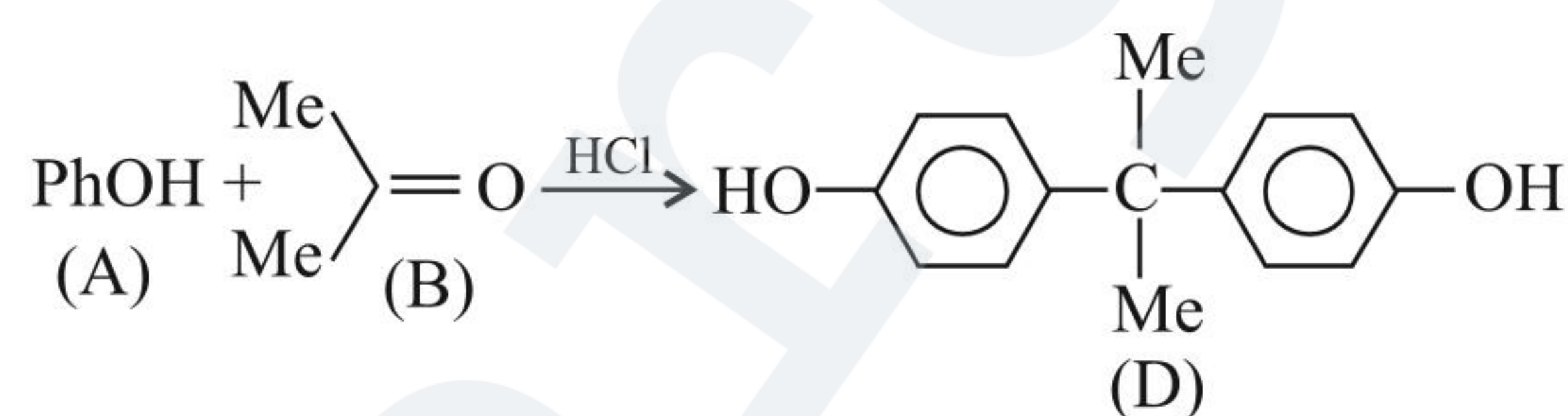
Exercise 4.1

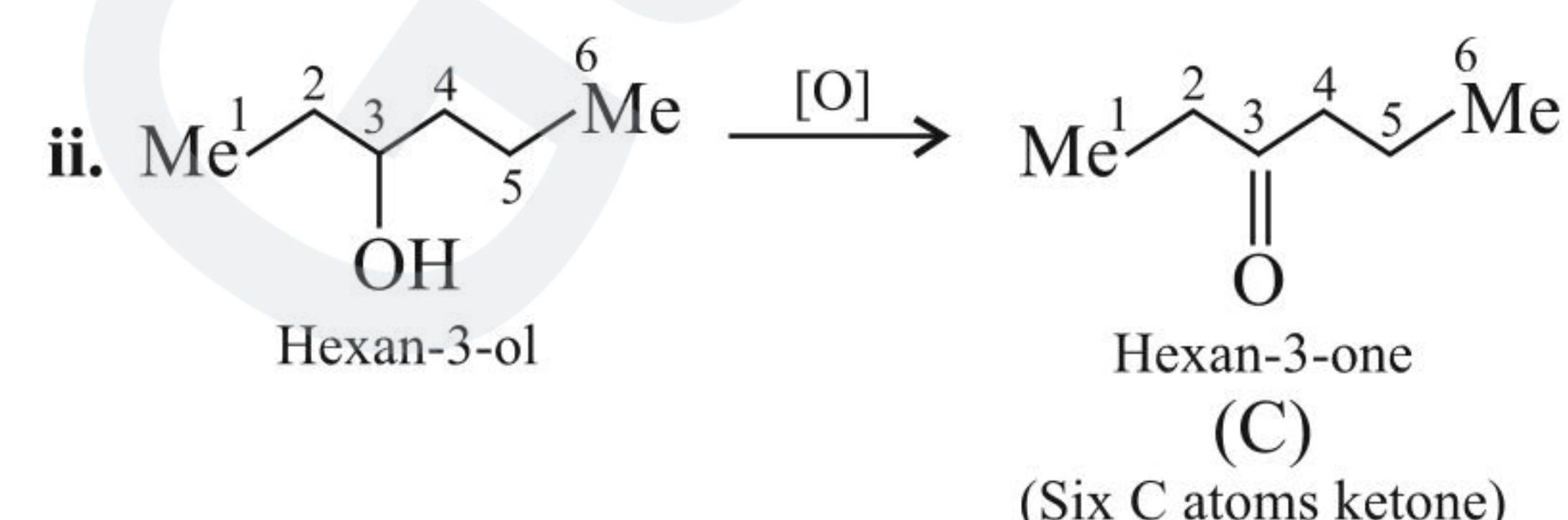


The hemiacetal



while electrophilic substitution of phenols by carbonyl compound in H^+ gives irreversibly formed product (I) which further reacts with phenol to give (C).





- iii. The formation of (C) suggests that (A) has same skeleton as in (C) with (CH₂=) group replacing O.

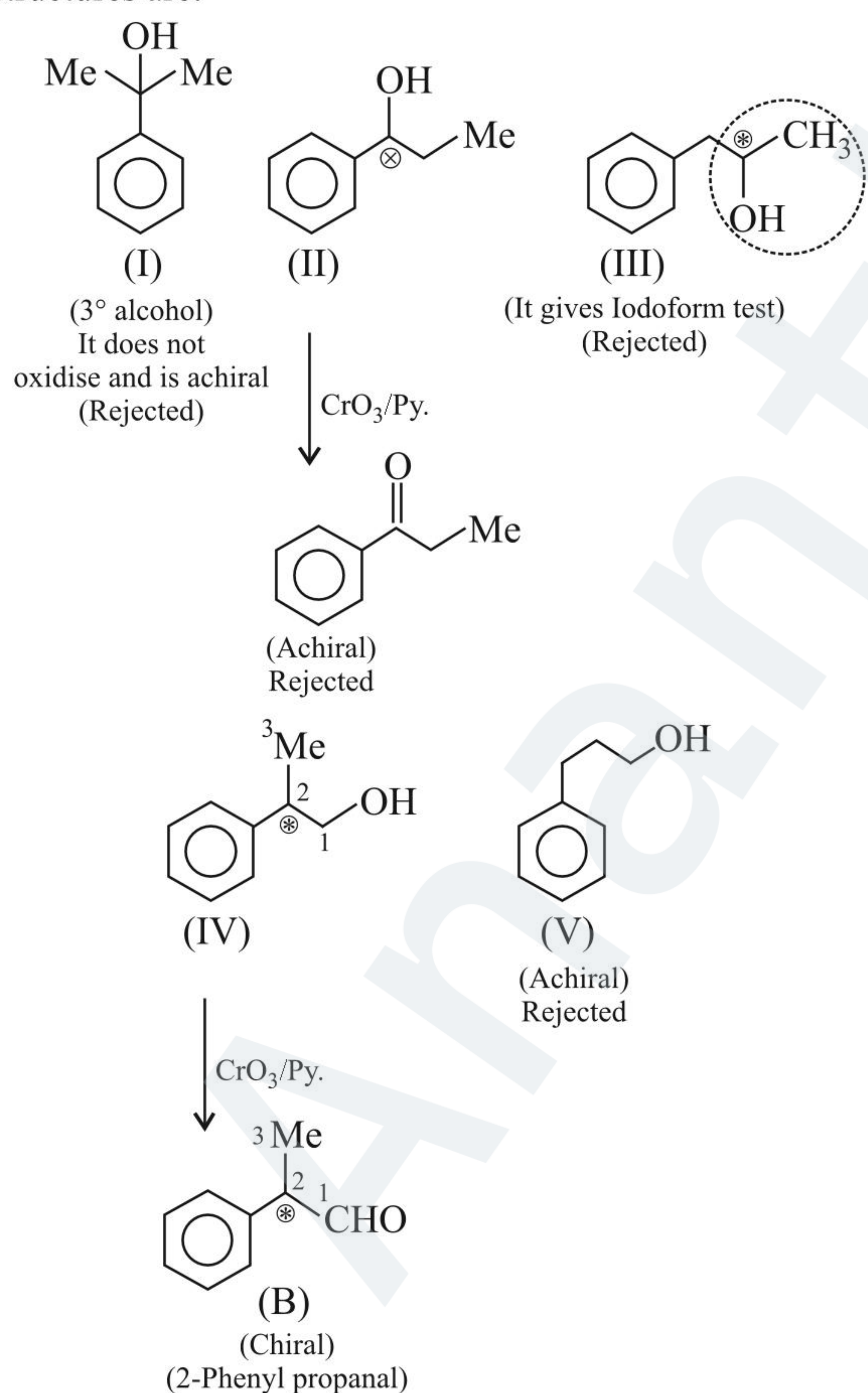
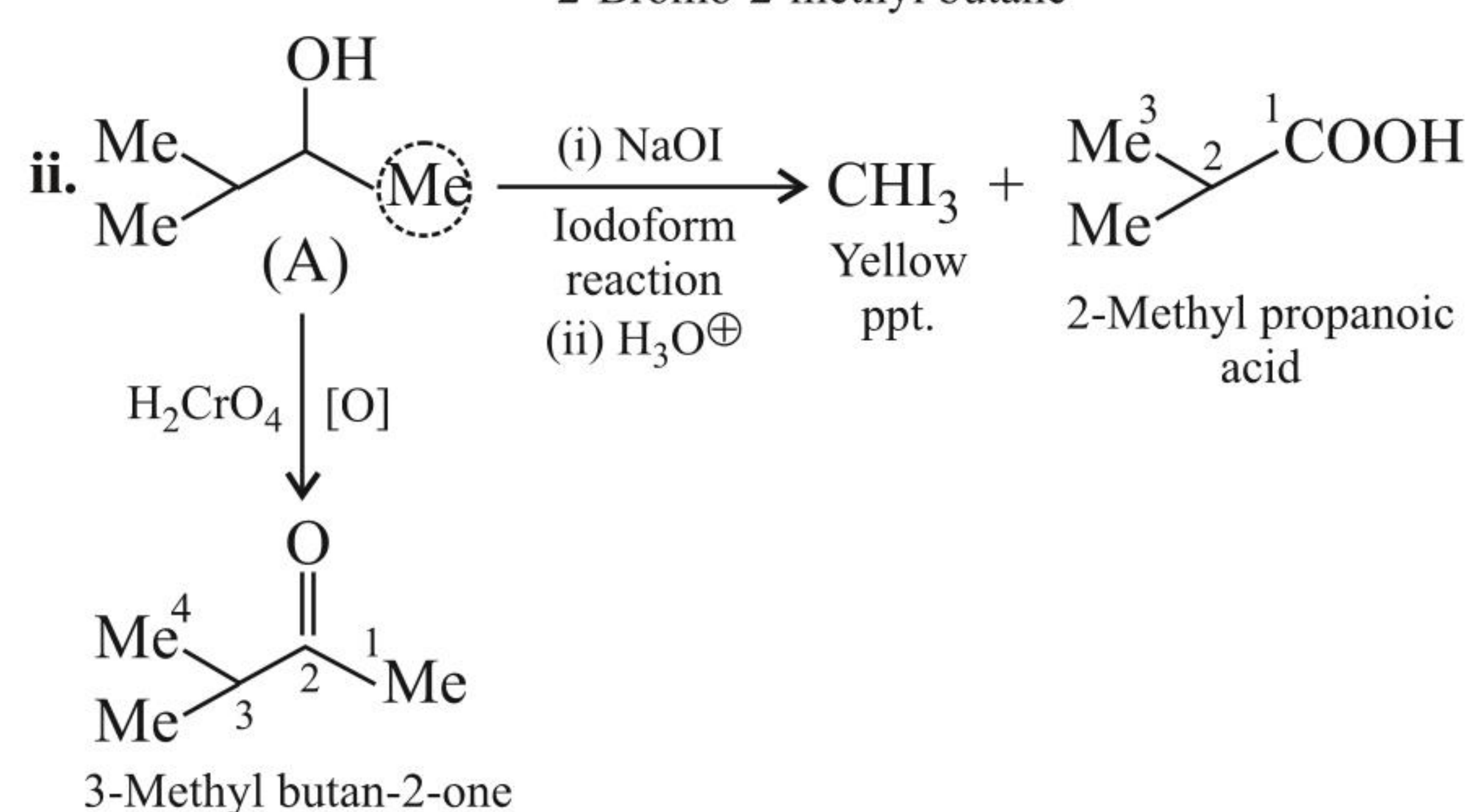
i.

(A)
2° ROH
3-Methyl butane-2-ol

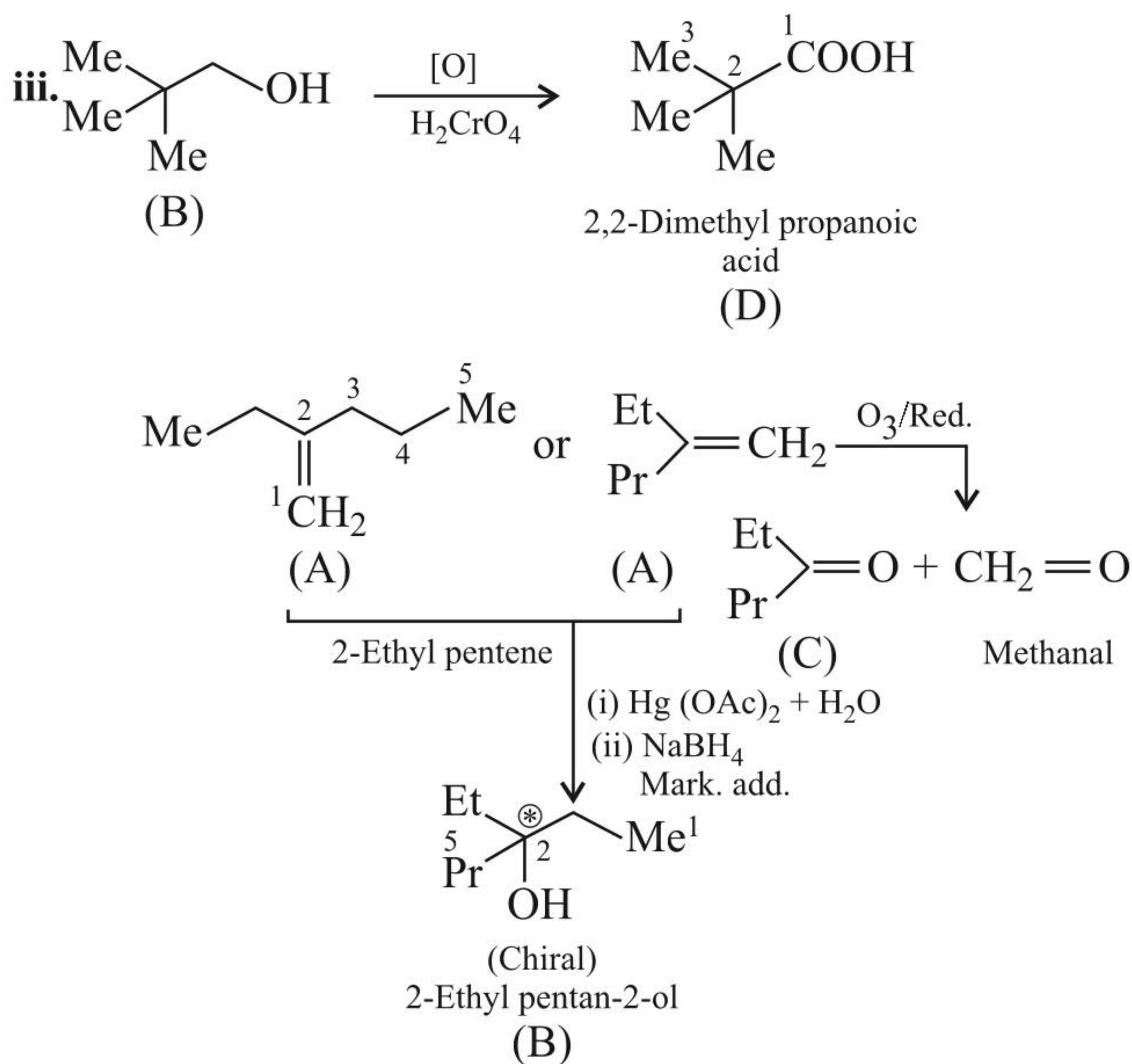
(B)
1° ROH
2,2-Dimethyl
propan-1-ol

(C)
3° ROH
2-Methyl butan-2-ol

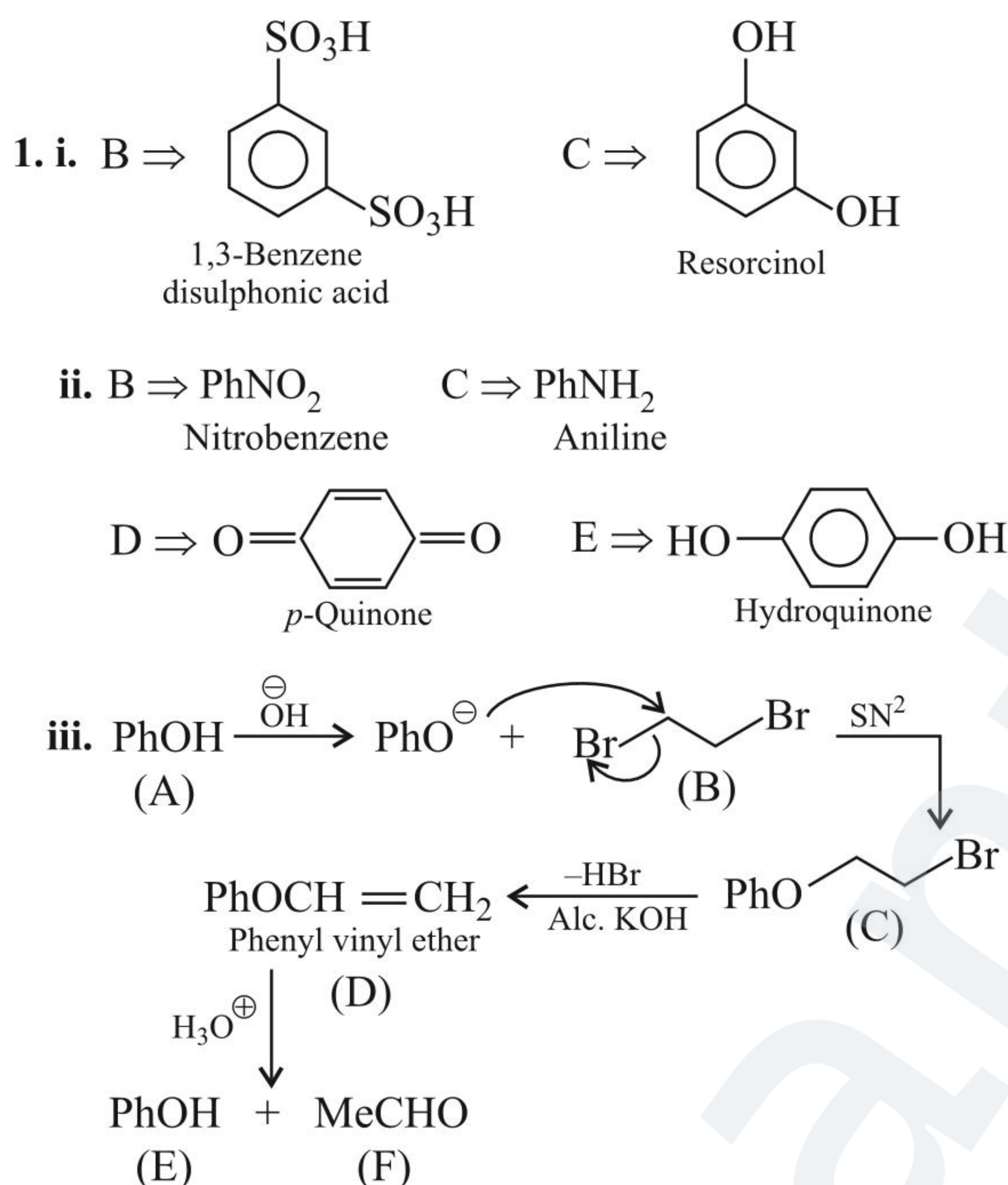
(E)
2-Bromo-2-methyl butane



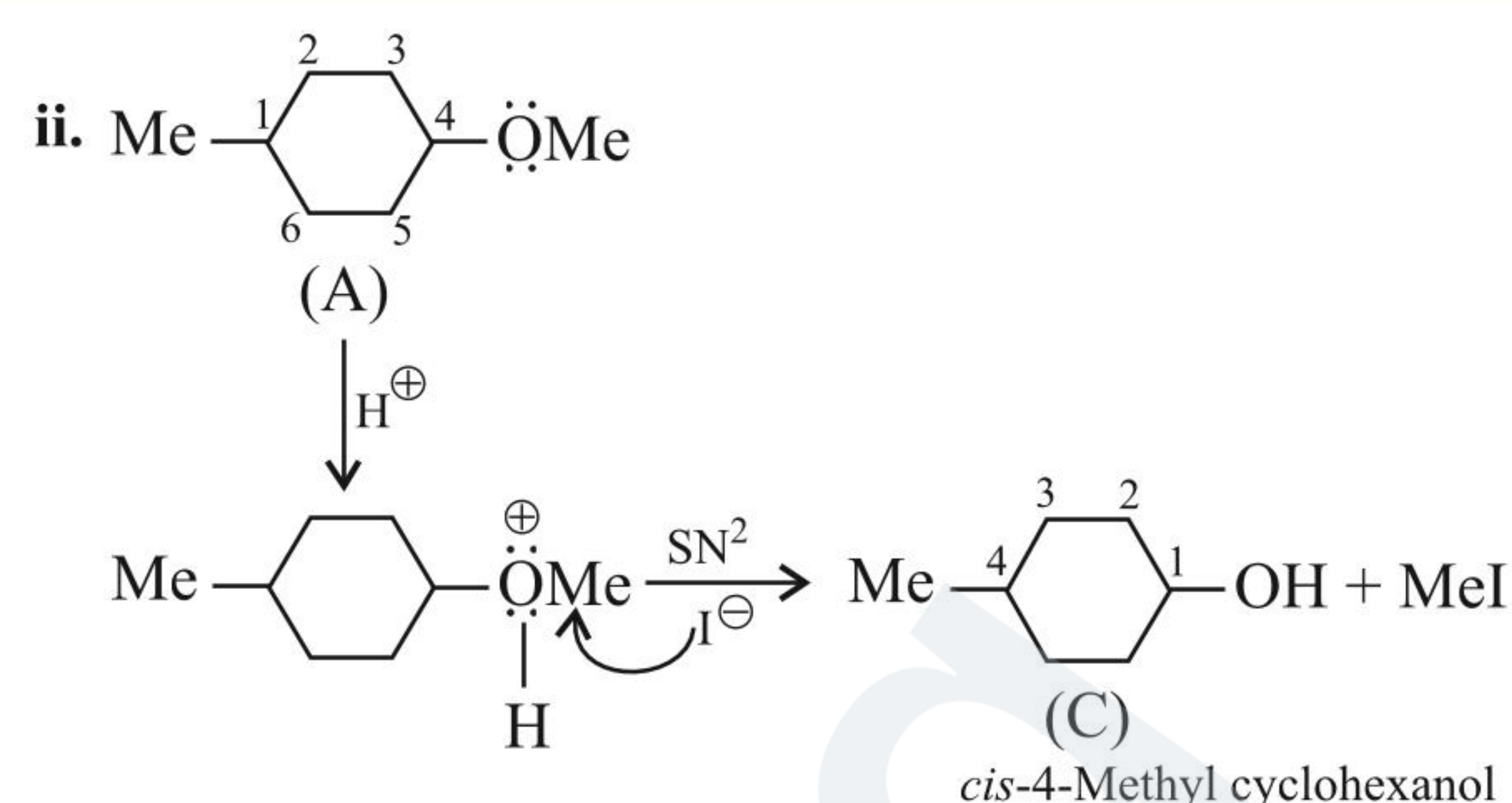
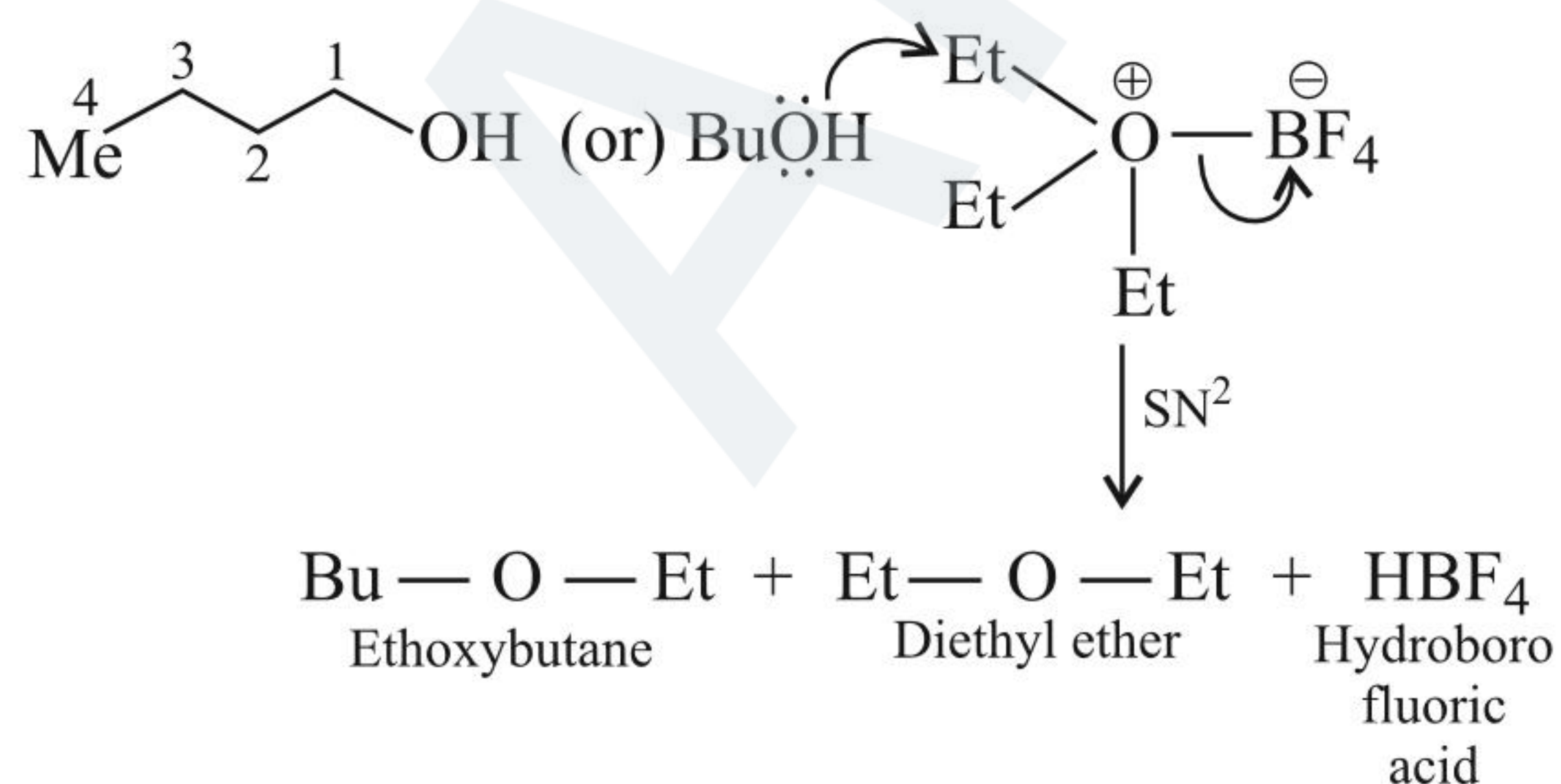
6. i. One DU in (A) and reaction with Br_2/CCl_4 suggest $(\text{C}=\text{C})$ group in (A).



Exercise 4.2

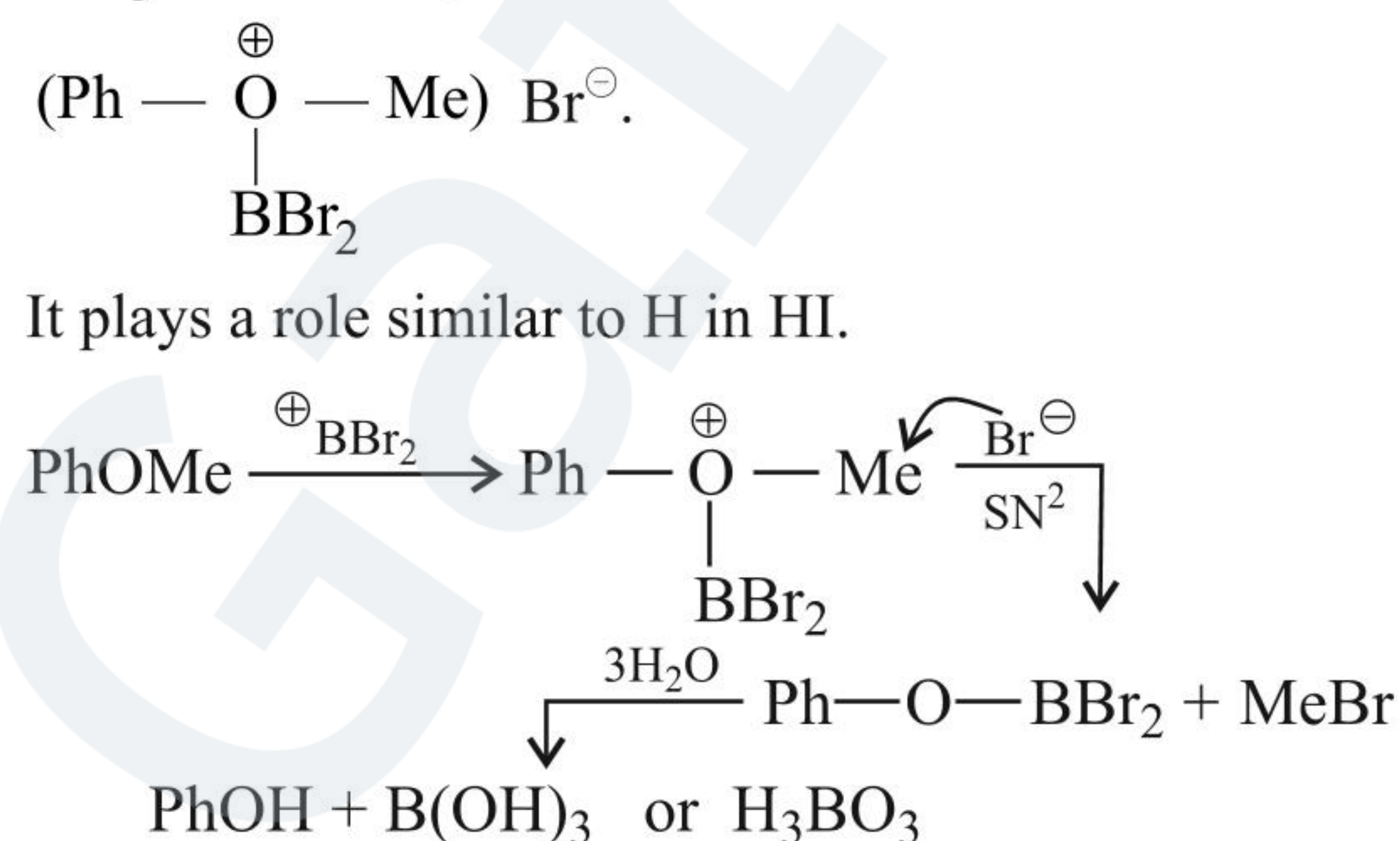


2. i. (B) (Trialkyloxonium salts) are good alkylating agents. S_N2 reaction occurs with the nucleophile ($\text{Bu}\ddot{\text{O}}\text{H}$) displacing Et_2O (a good leaving group).

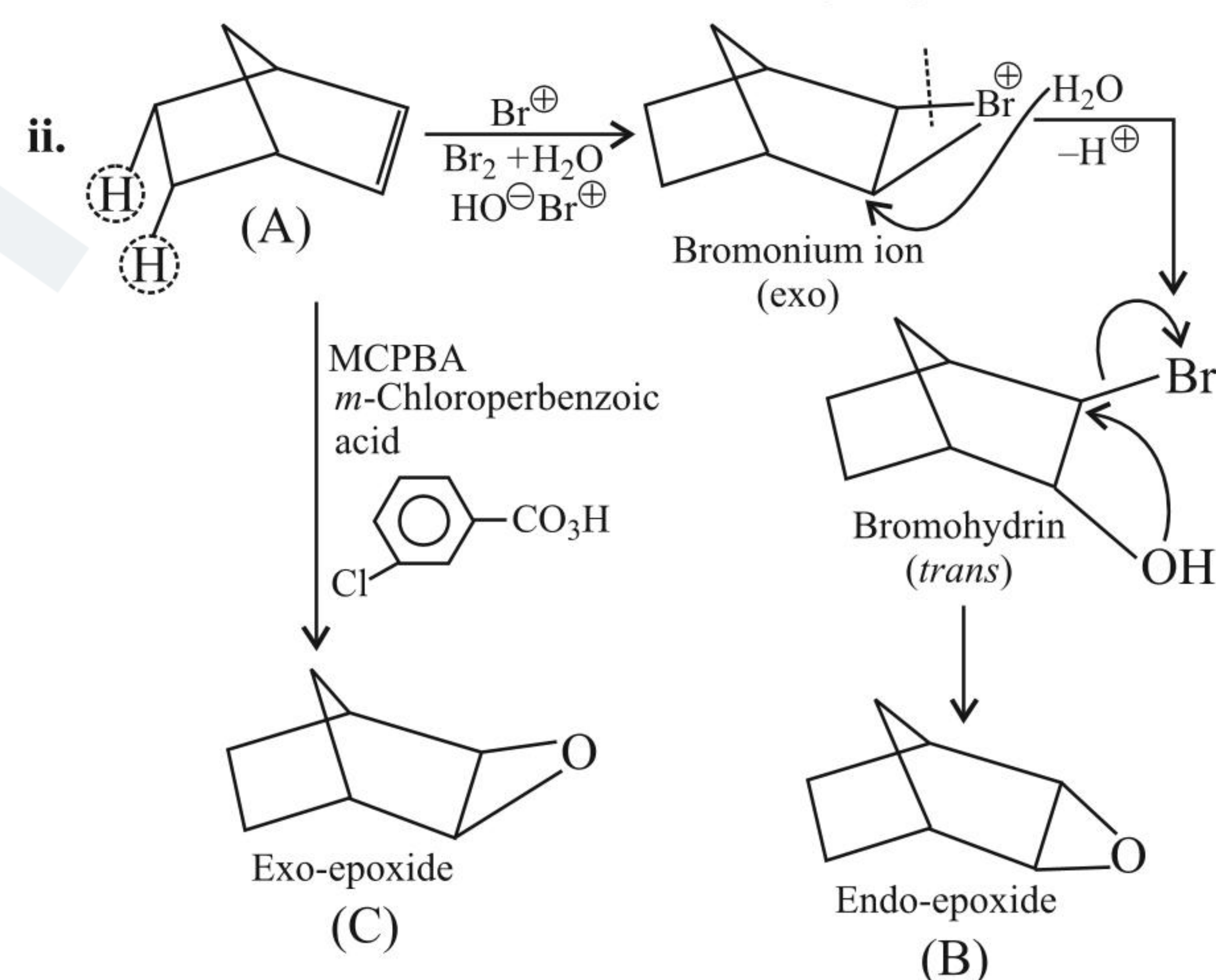


There is no change in the configuration of (C), i.e., retention of the configuration occurs since (C—O) bond is not broken.

3. i. BBr_3 forms complexes with the ether

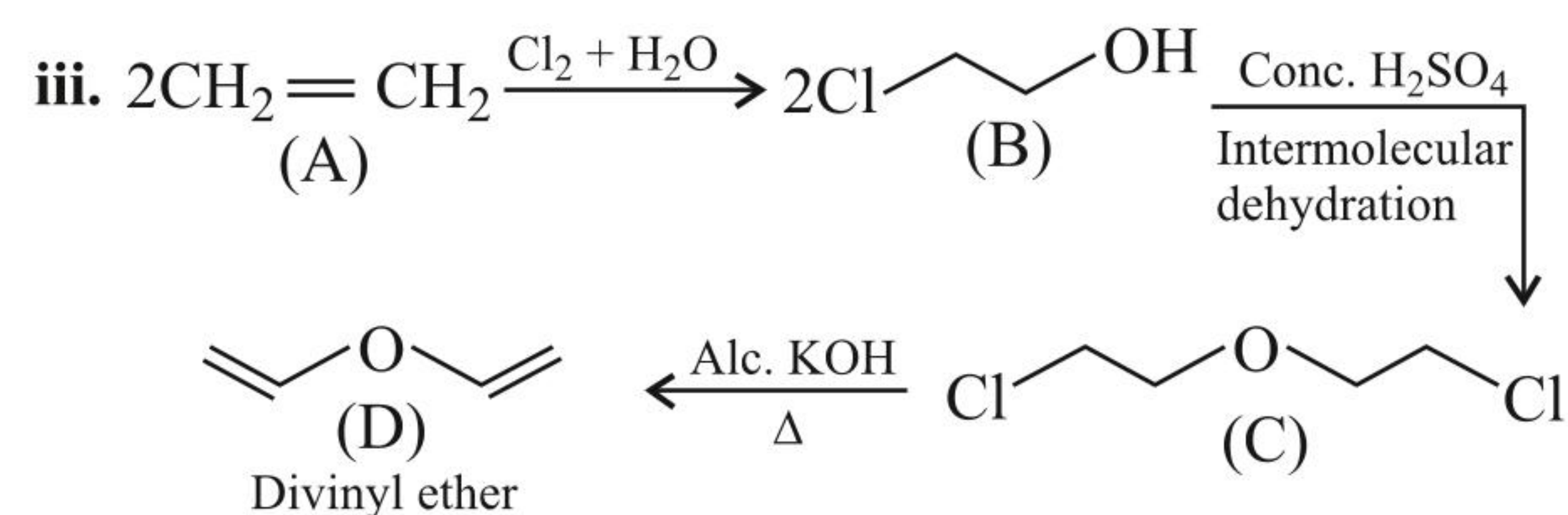


The products are: $\text{MeBr} + \text{PhOH} + \text{H}_3\text{BO}_3$.

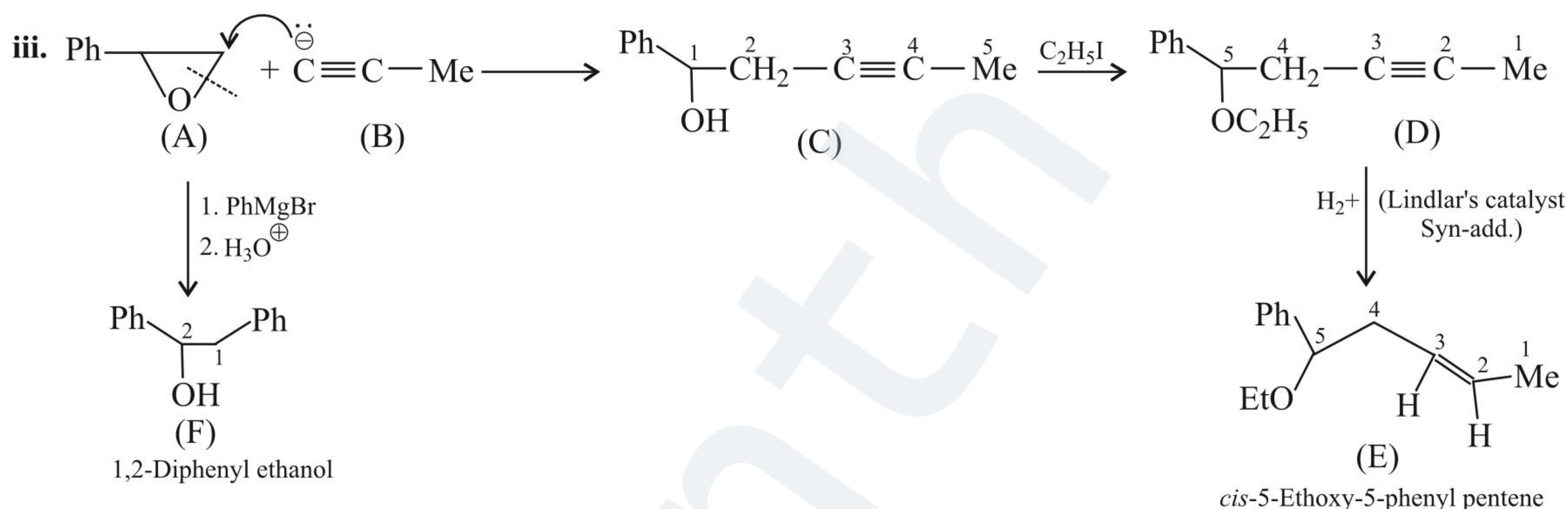
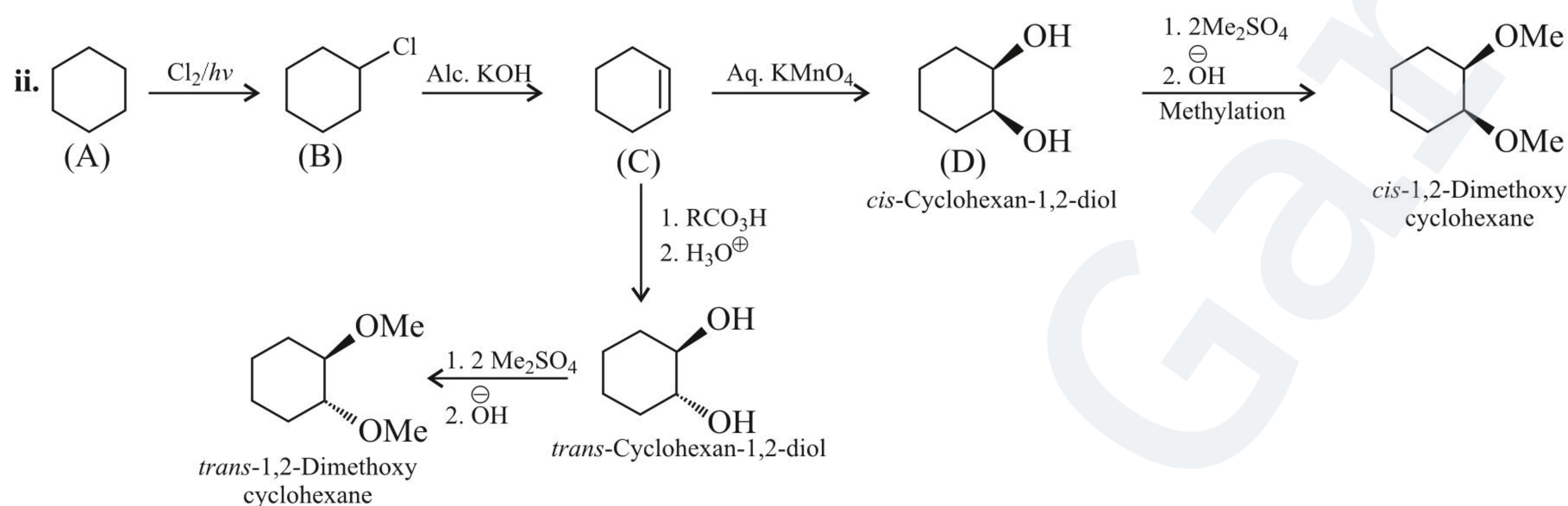
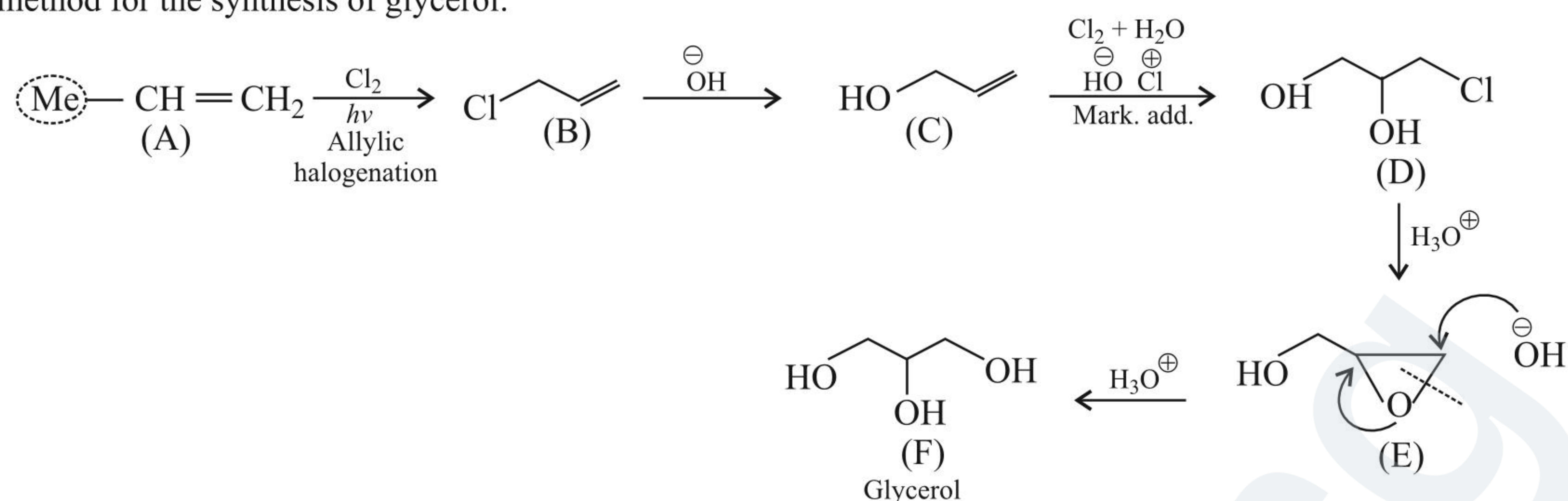
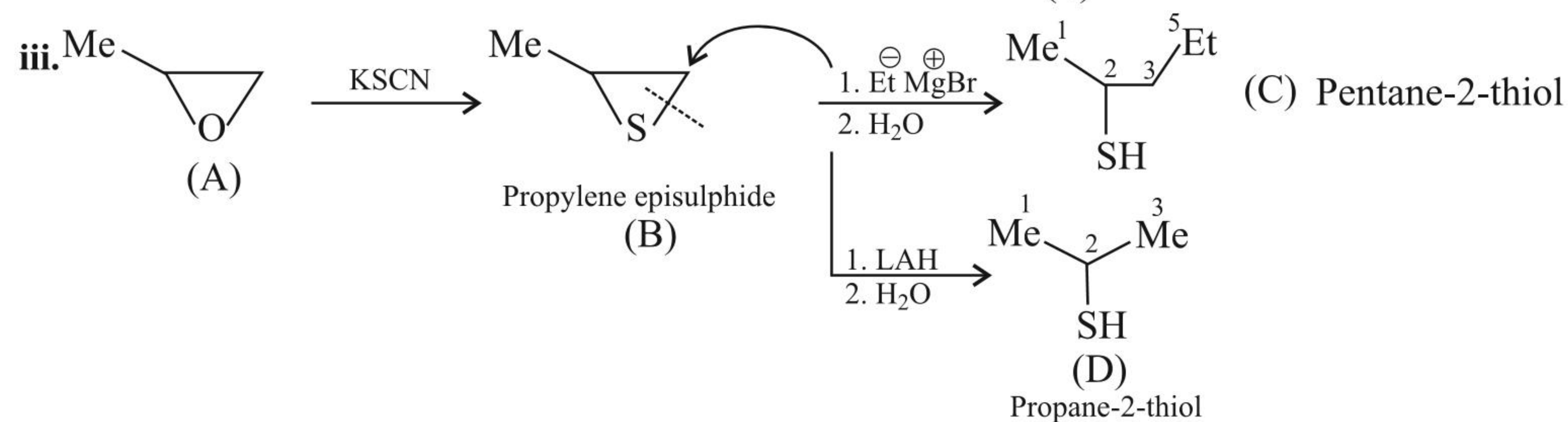
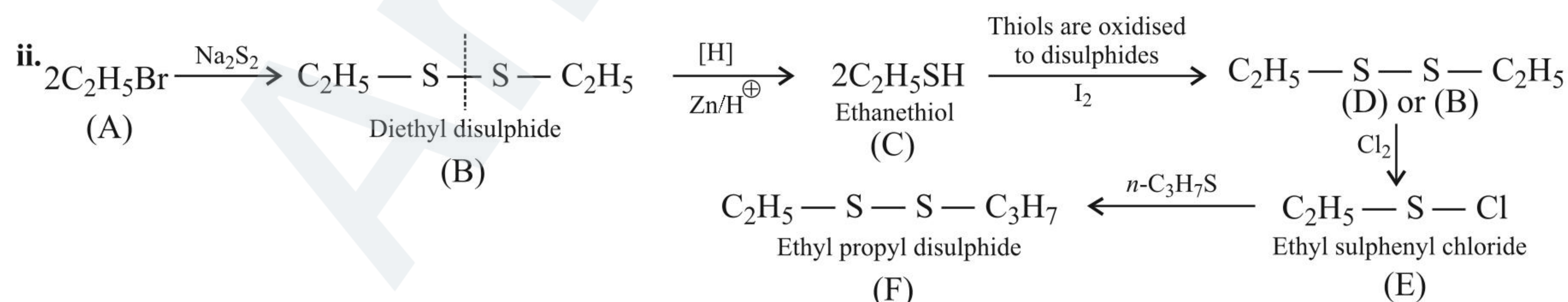
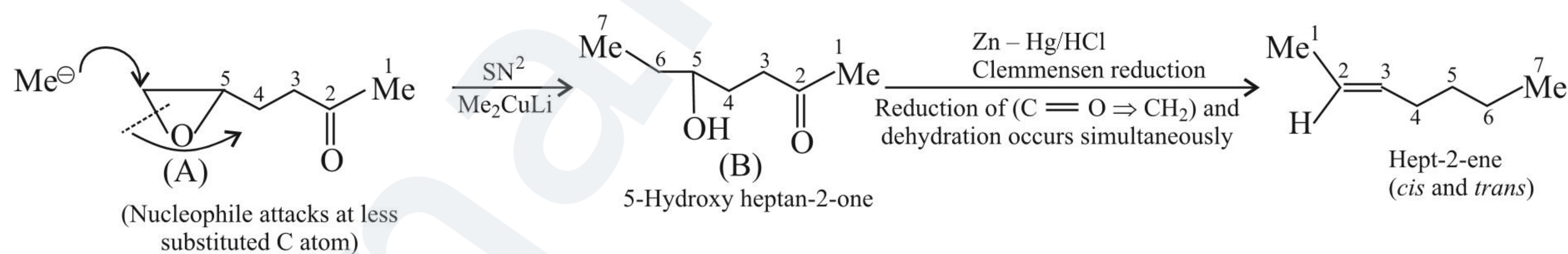


In (A), the axial-like encircled H atoms hinder the endo approach (same side) by bulky MCPBA, so it approaches from other side, giving exo-epoxide (C).

The intermediate bromonium ion is also *exo*. It is opened by an attack with H_2O from the *endo* side, giving a *trans*-bromohydrin with the (OH) *endo*, which can give only *endo* epoxide (B).



4. i. Commercial method for the synthesis of glycerol:

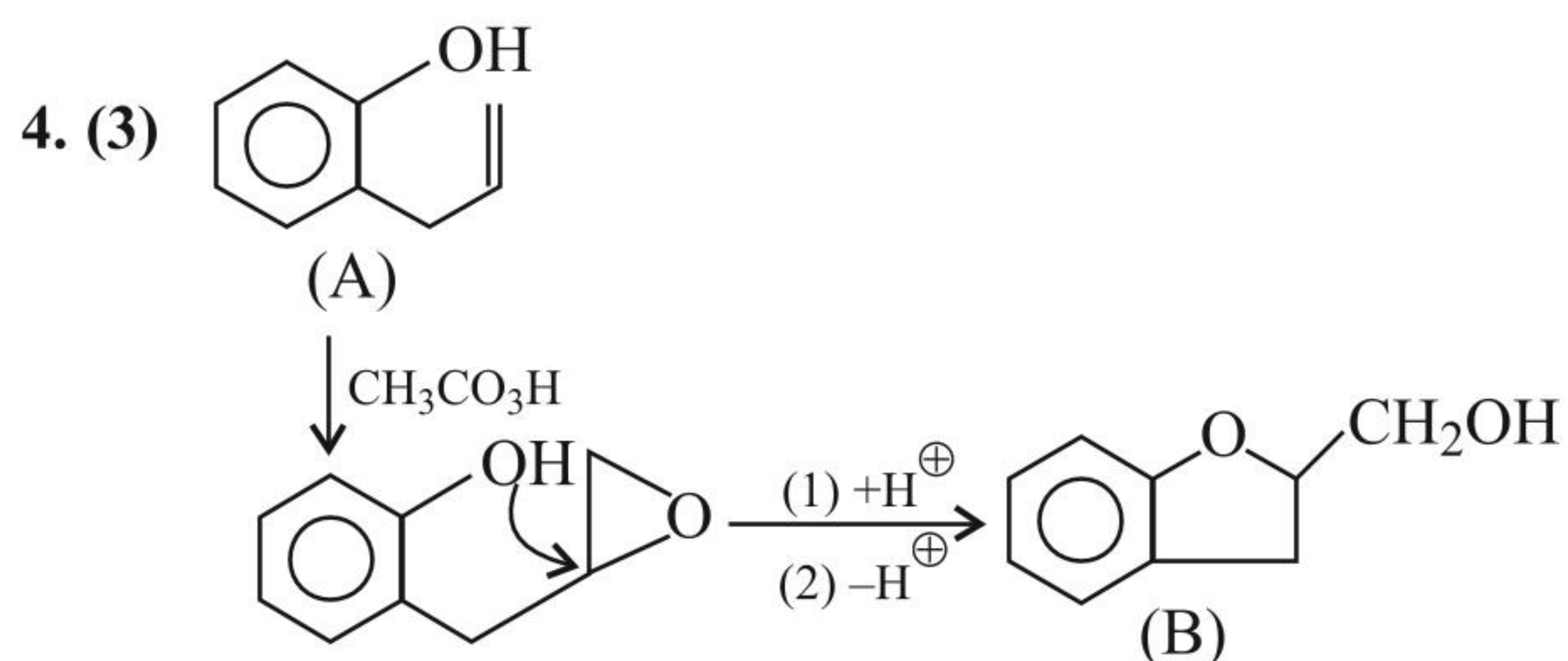
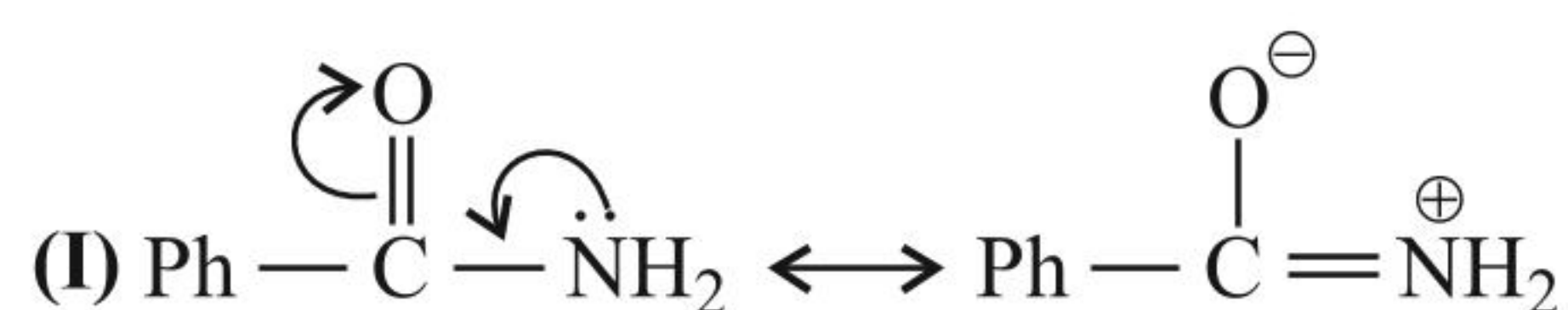
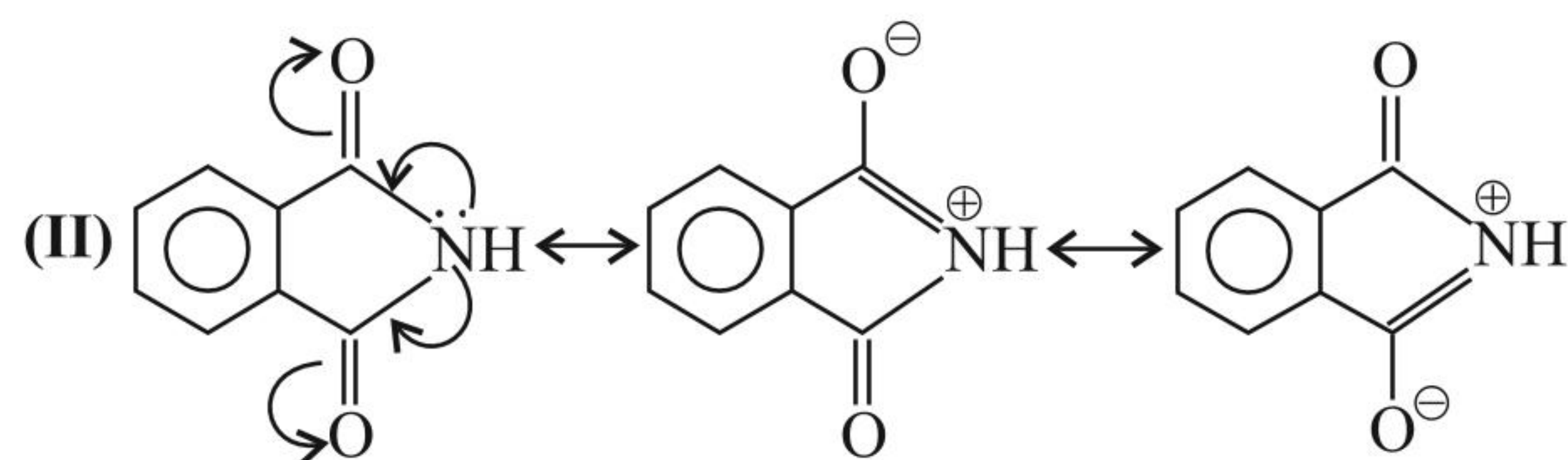
5. i. Dialkyl lithium cuprate is less reactive than Grignard reagent, hence (C=O) group is not reduced by R_2CuLi .

Exercises

Single Correct Answer Type

1. (2) Acid (II) > Ester (III) > Alcohol (I) > Ketone (IV).
 2. (3) Acid (IV) > Phenol (II) > Alcohols (I) > Alkyne (III).
 3. (1) Due to two \bar{e} -withdrawing ($C=O$) groups in (II), it is more acidic than (I) (one EW ($C=O$) group).

Moreover, (II) is much more resonance stabilised than (I).



5. (1) The positive charge that develops on benzylic C in this S_N1 reaction is most effectively delocalised by (OMe) group (+R and -I). The ($p\text{-NO}_2$) group withdraws \bar{e} density from the ring by -I and -R. ($p\text{-Cl}$) group withdraws \bar{e} 's from the ring by -I only.

More EDG (e.g., -OMe) stabilises positive charge on the benzylic C atom, whereas EWG (e.g., $-\text{NO}_2$, $-\text{Cl}$) destabilises the positive charge. Hence, the reactivity order is:

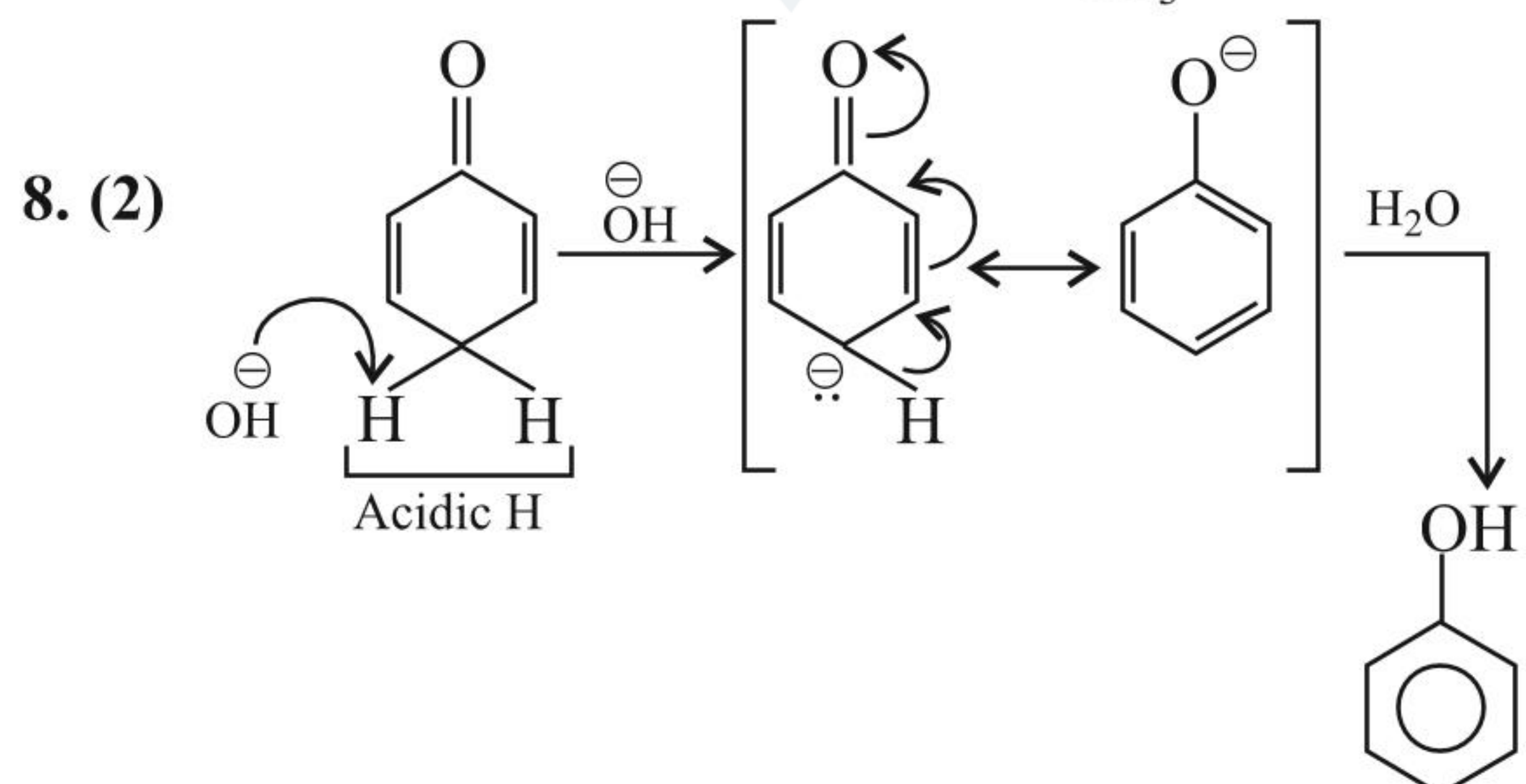
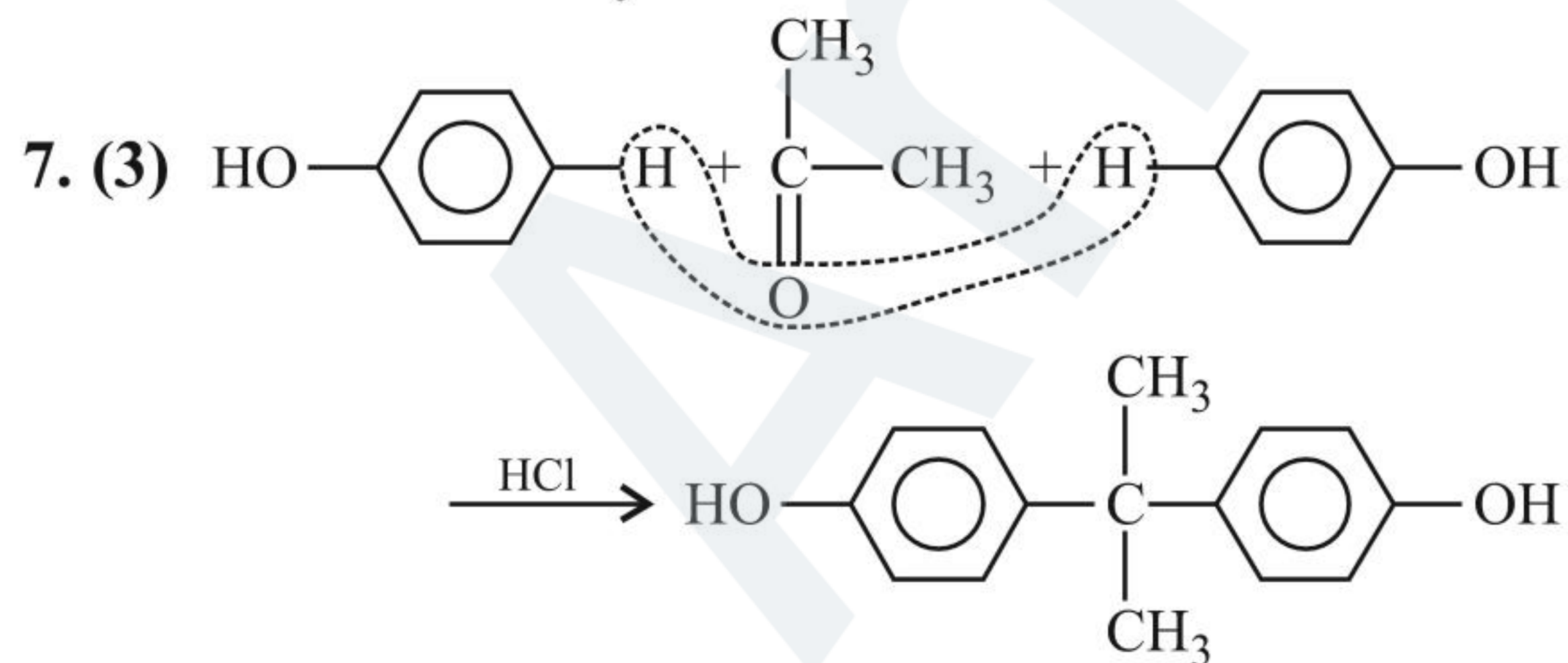
I > II > III > IV.

6. (3) EDG favours S_N1 reactivity with HBr (as explained in Q. No. 5). EWG retards S_N1 reactivity with HBr.

ED effect of (-OMe) (+R, -I) is greater than (Me) group (+I and H.C.). So, reactivity of III > II.

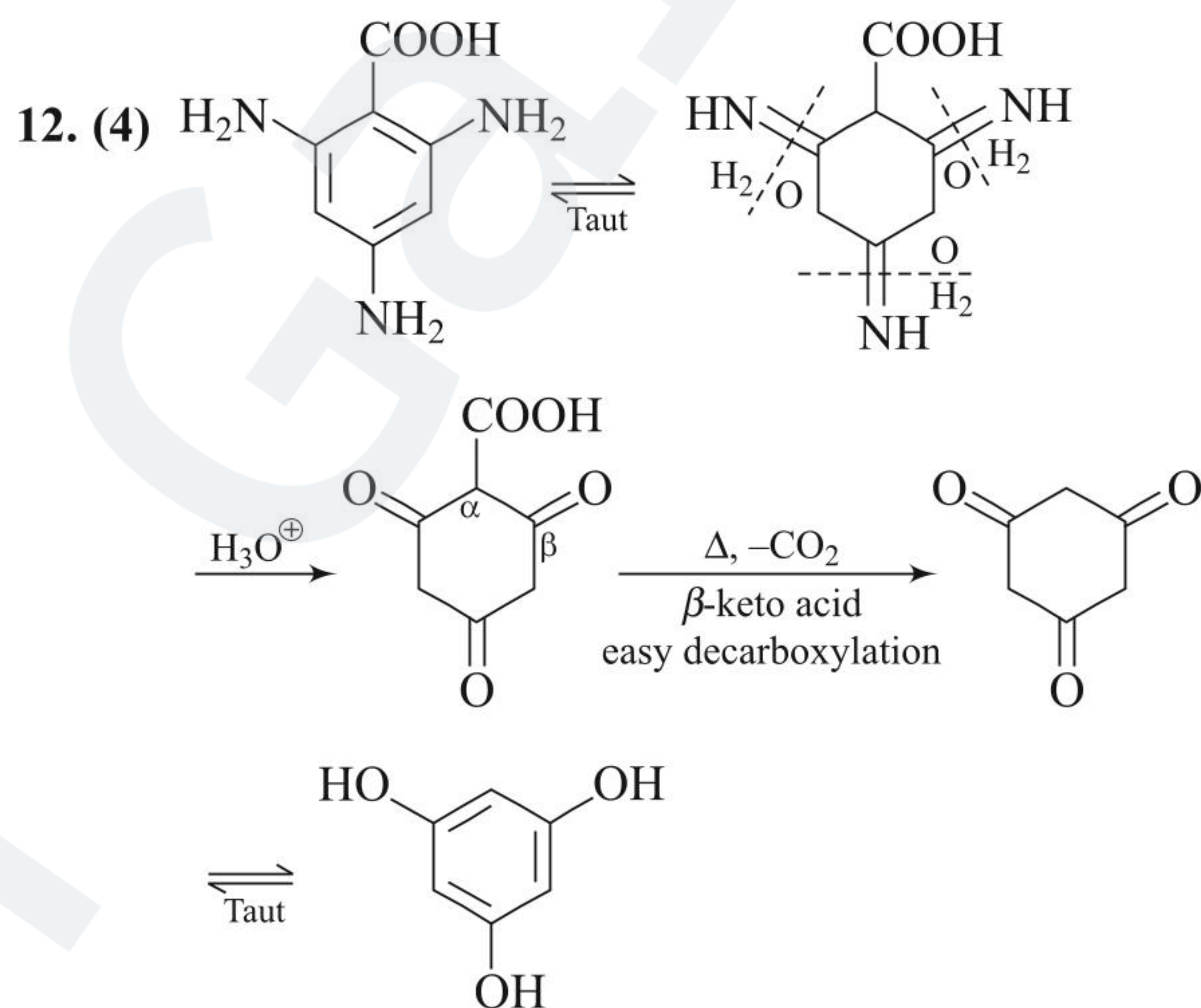
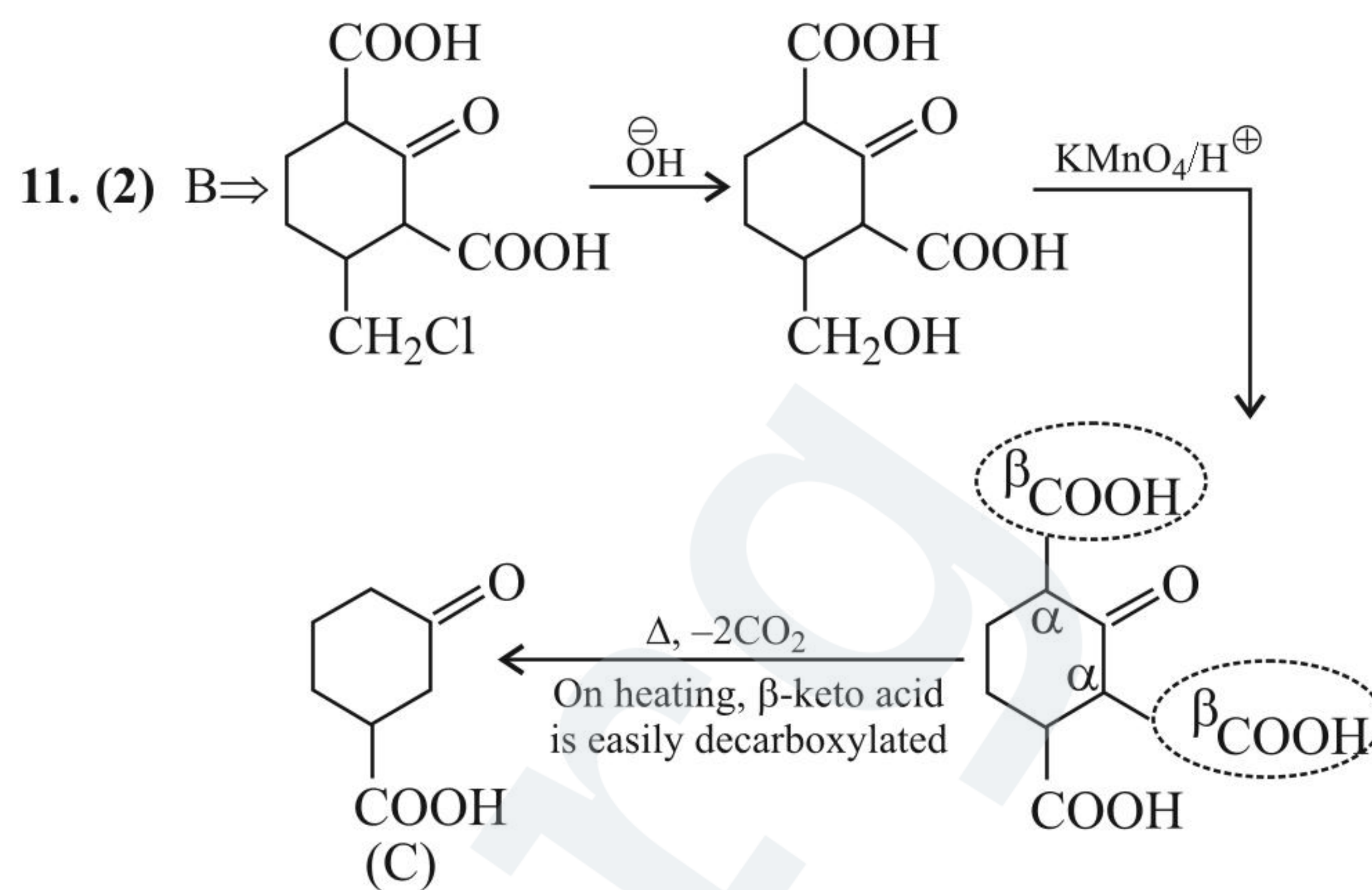
In (IV), (-OMe) group is at m -position and exerts only -I effect and so reactivity of (IV) is less than (I).

So the reactivity order is: III > II > I > IV.



9. (4)

10. (3)

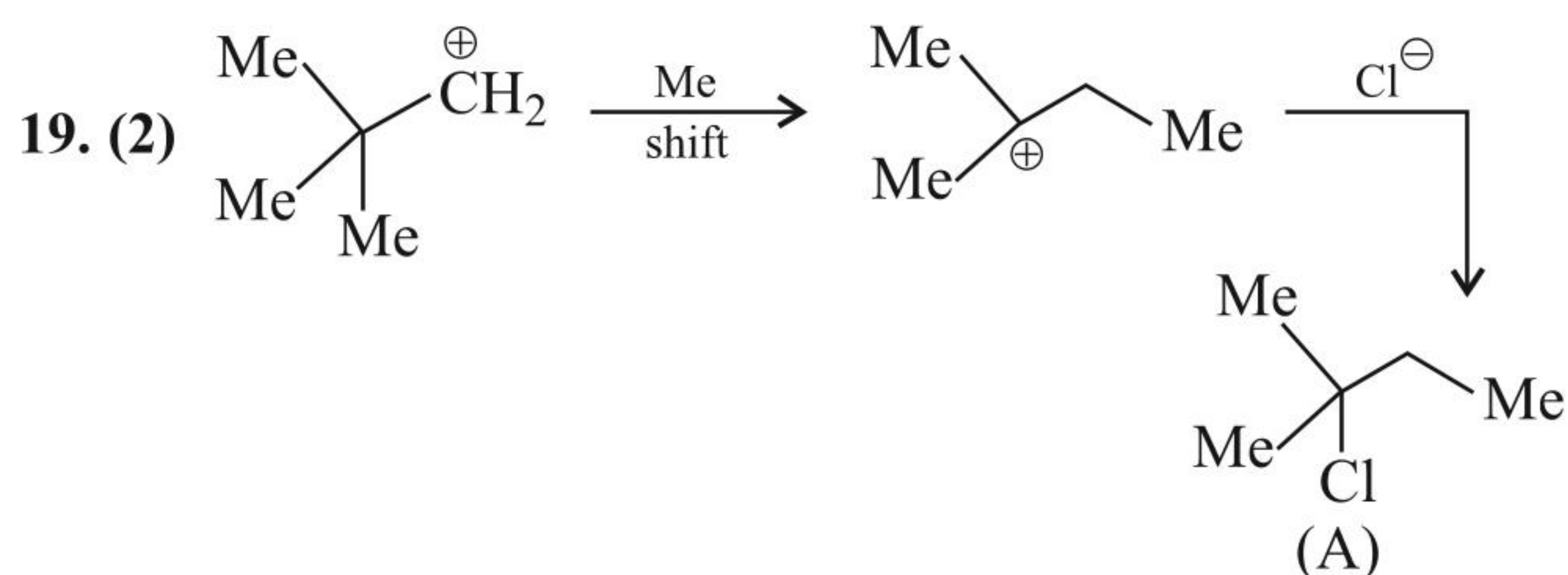
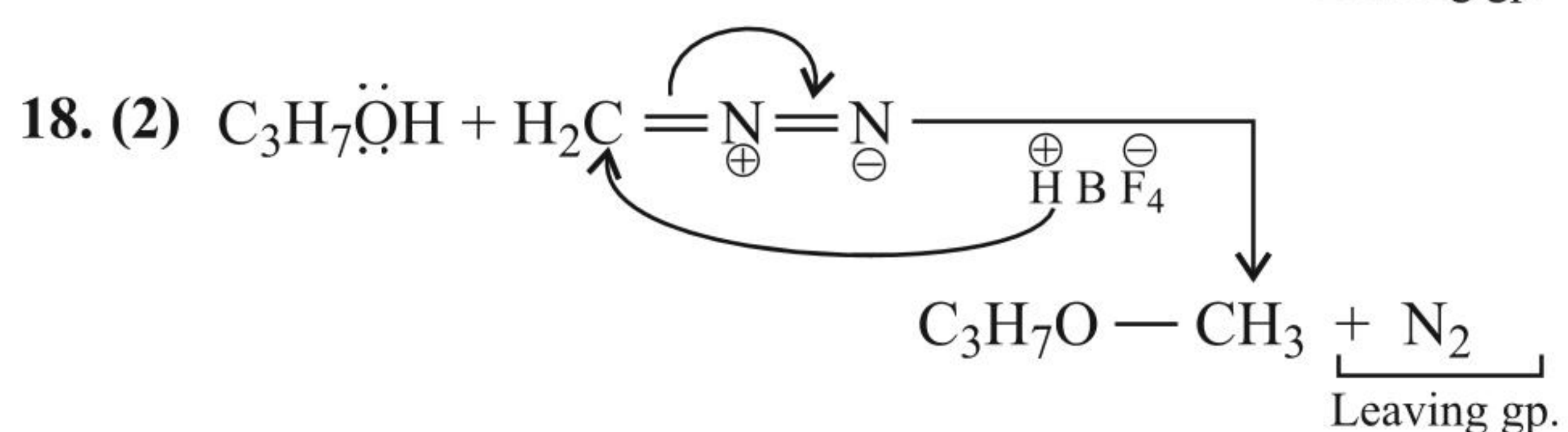
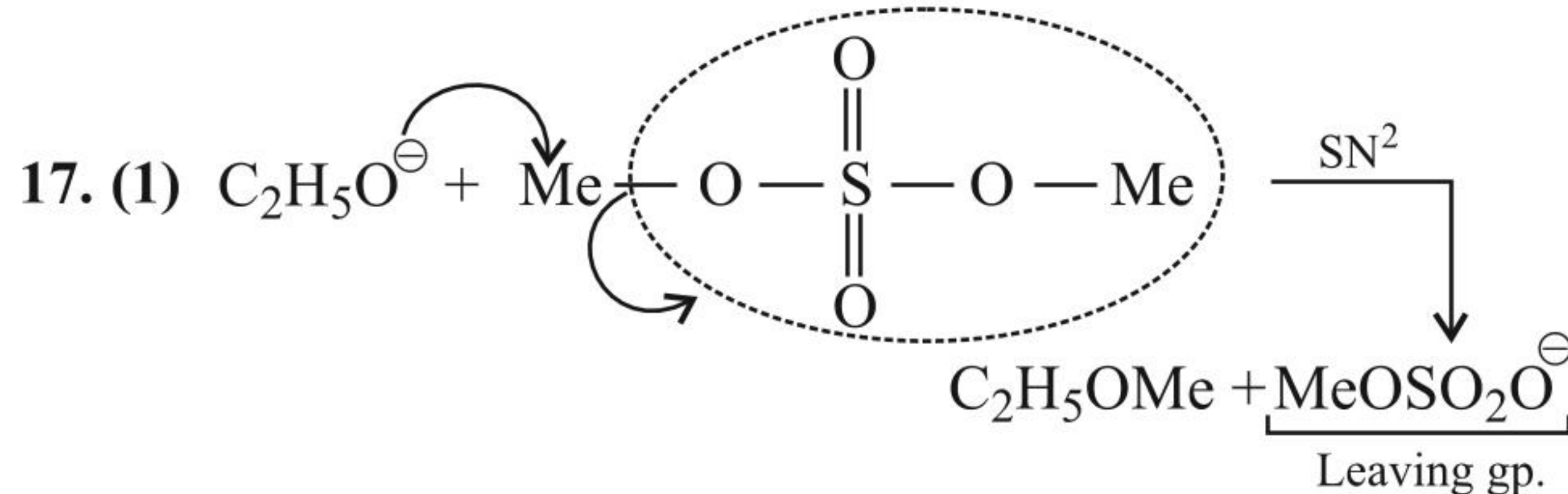


13. (4) Method (3) would give rearranged product also. It would give a mixture of 2-bromo and 3-bromo pentane. In methods (1) and (2), no rearrangement occurs and it gives (B) exclusively. The tosyl group, a good leaving group, is then easily displaced by reaction with Br^- in an S_N2 reaction.

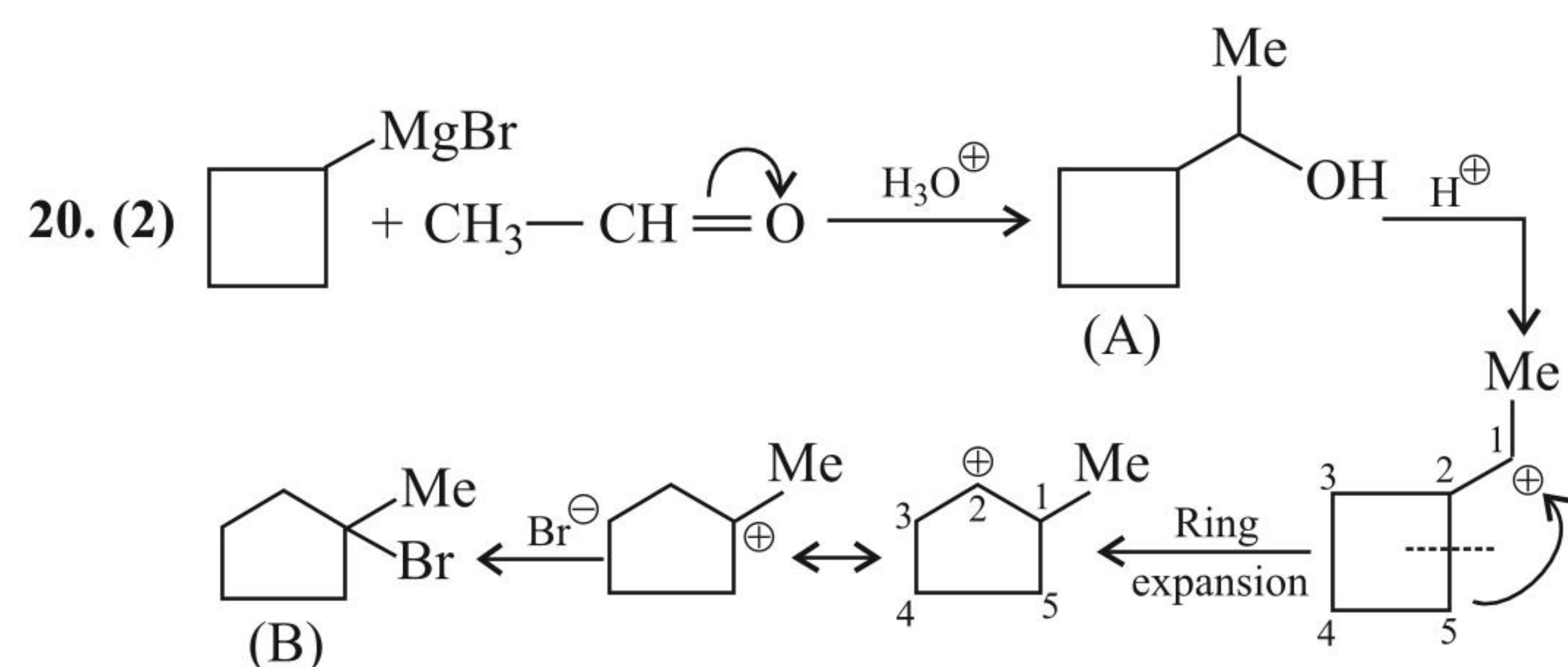
14. (4)

15. (4)

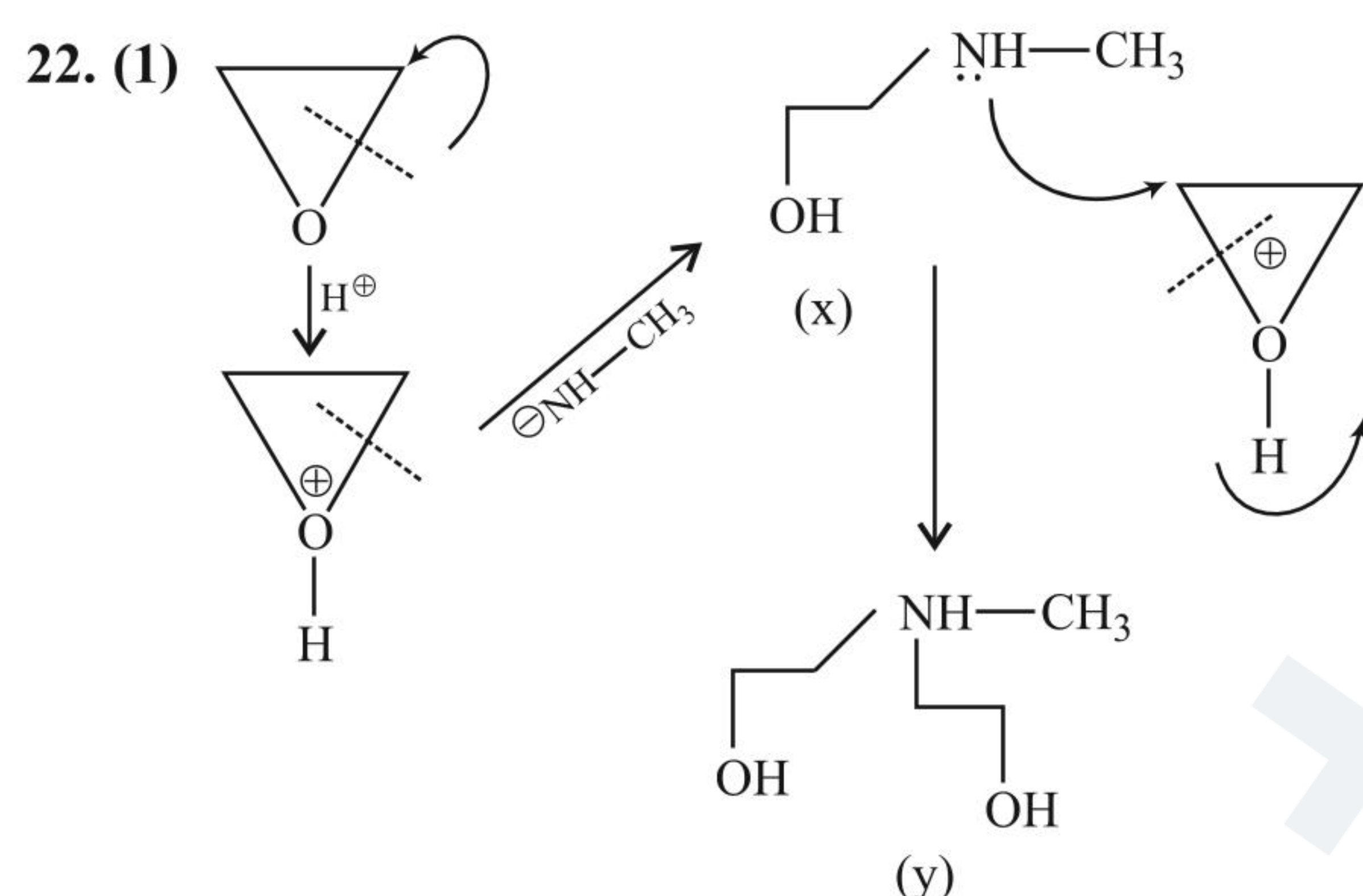
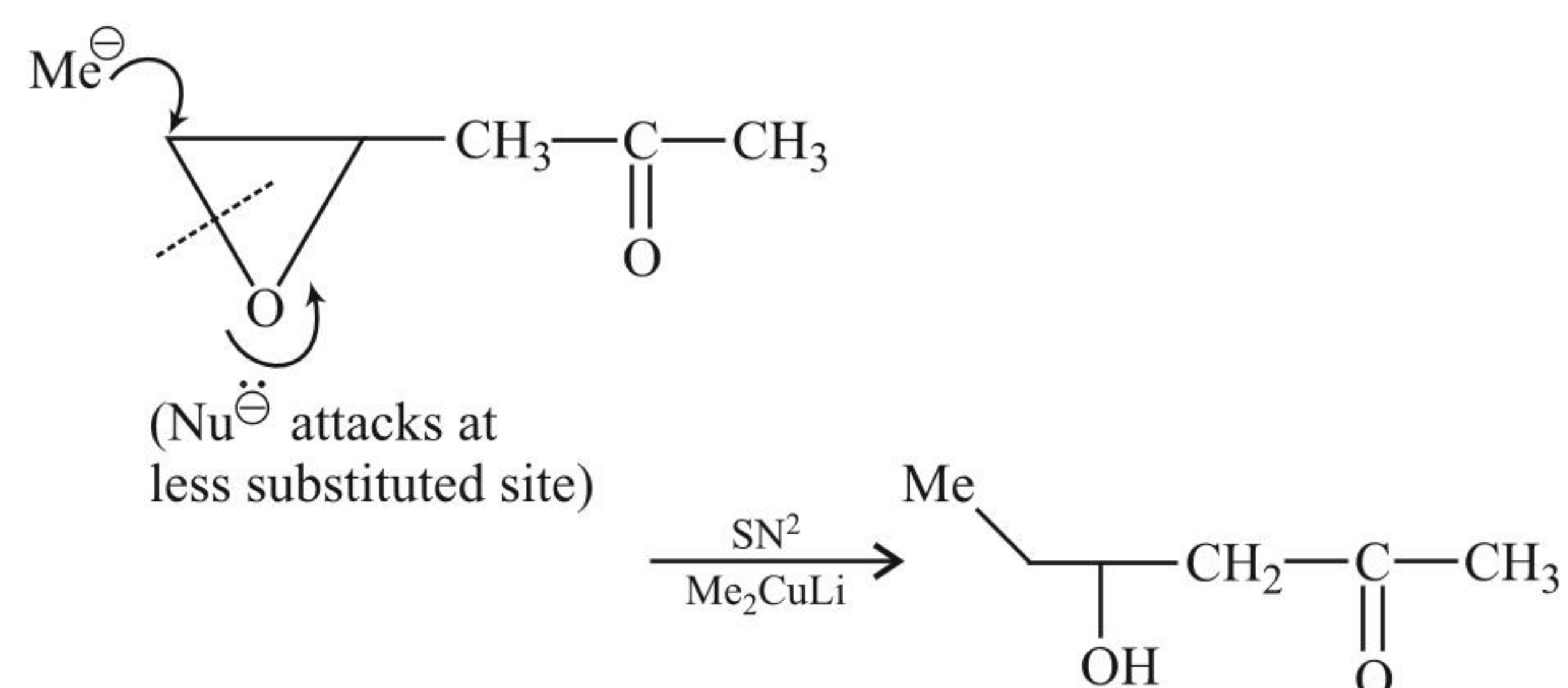
16. (2)



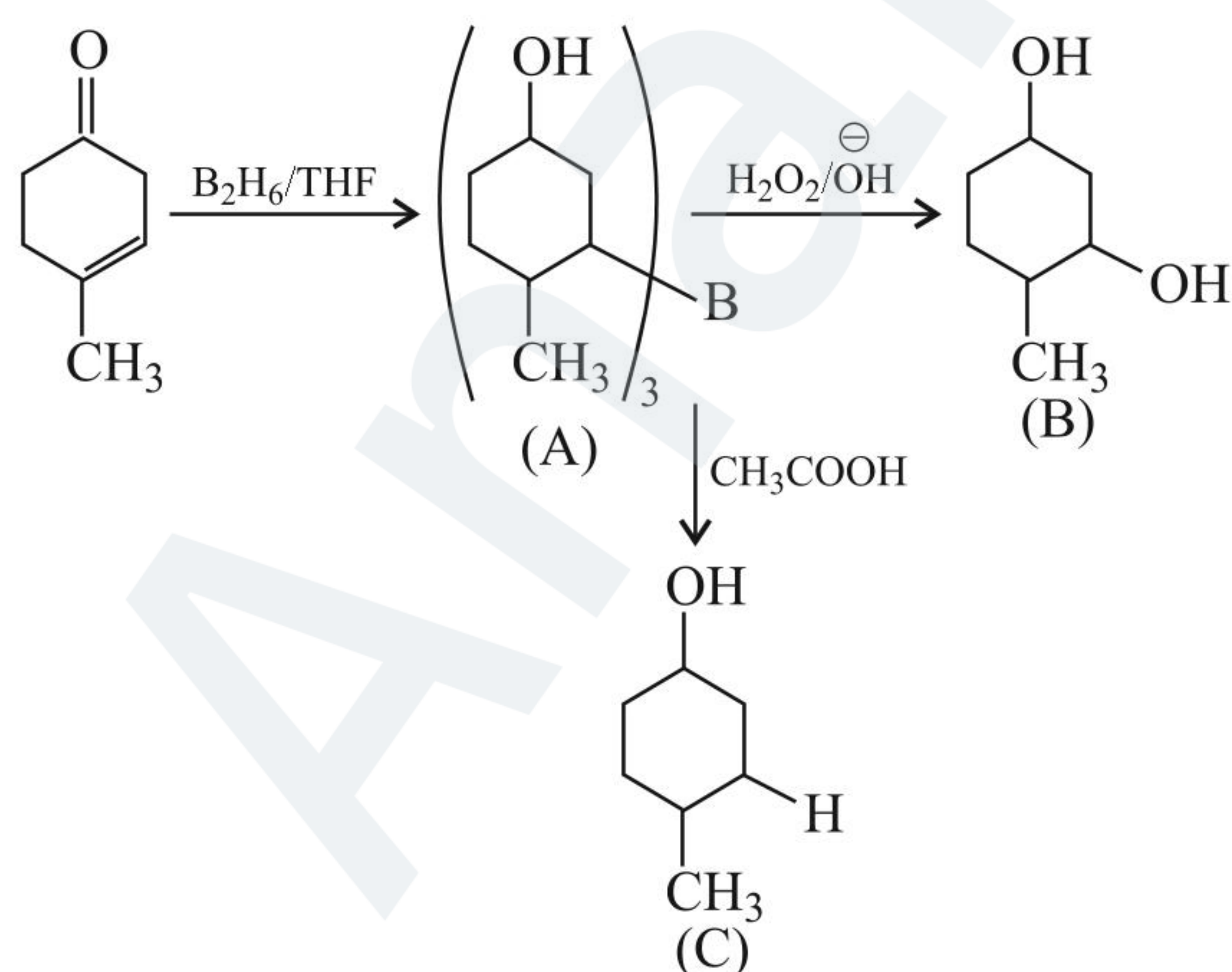
The formation of (B) does not involve carbocation formation and rearrangement, so the product (B) is $\text{Me}_3\text{CH}_2\text{Cl}$.



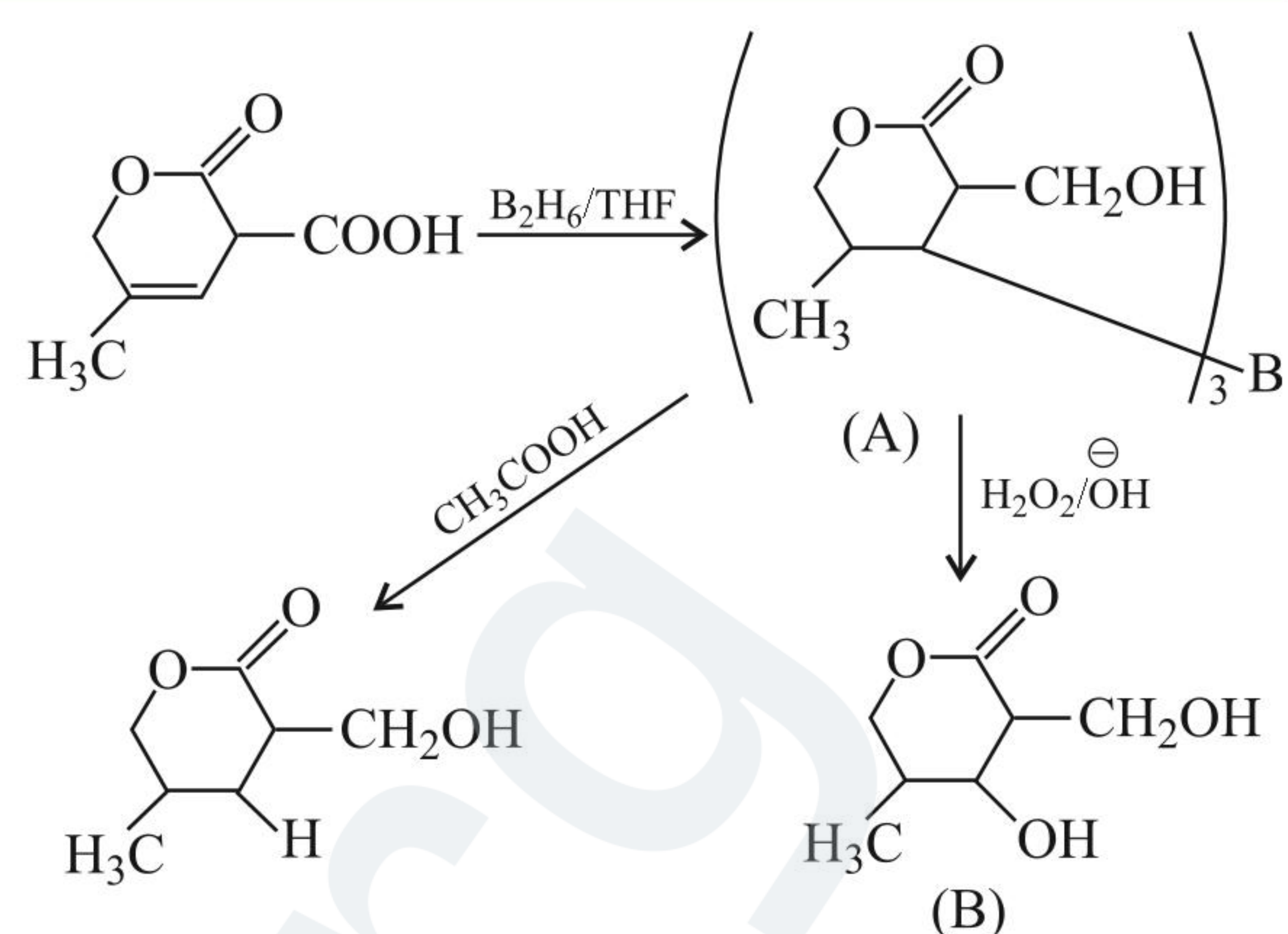
21. (1) Me_2CuLi is less reactive than Grignard reagent, hence $(\text{C}=\text{O})$ group is not reduced.



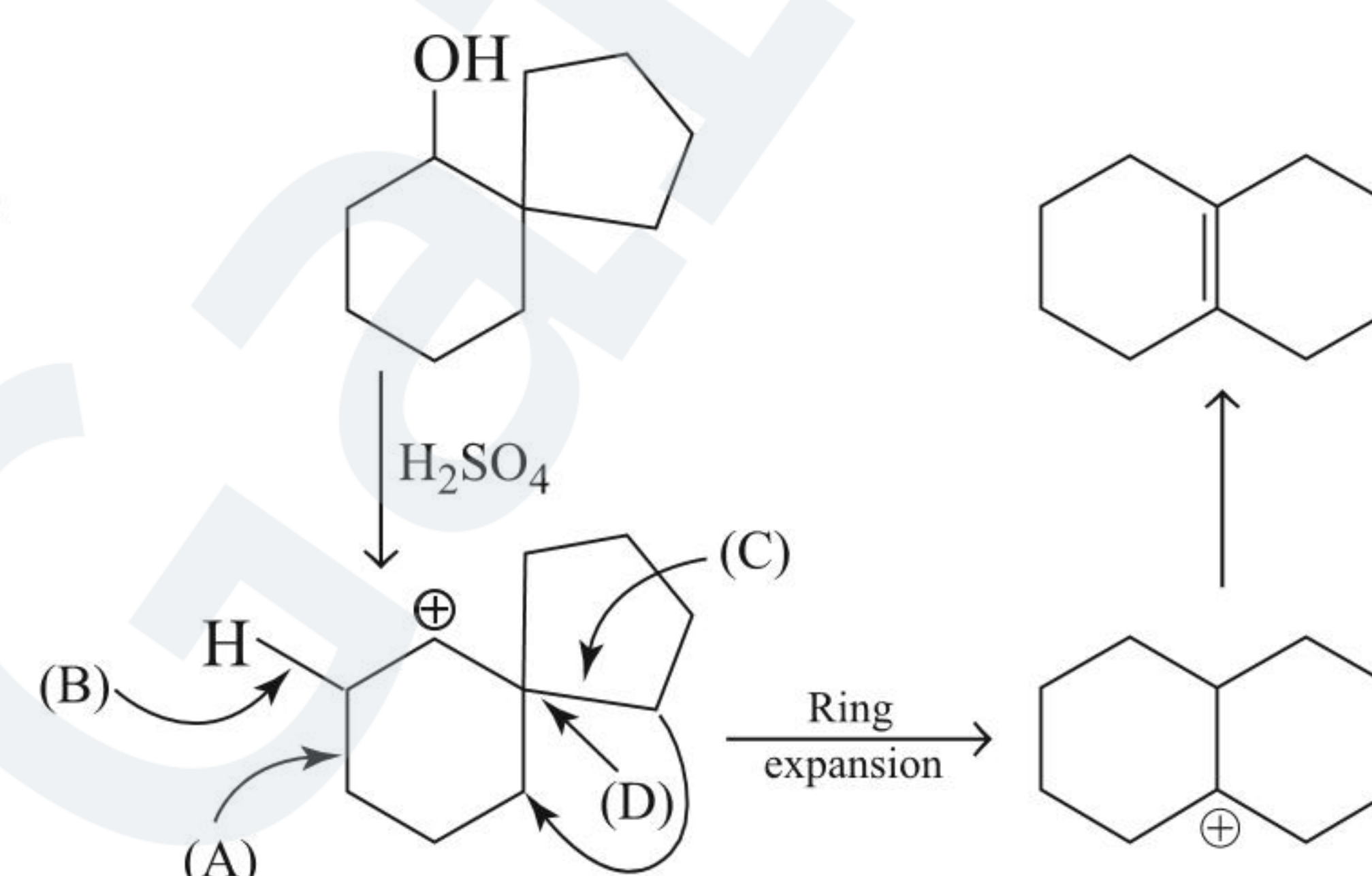
23. (1) $\text{B}_2\text{H}_6/\text{THF}$ also reduces $(\text{C}=\text{O})$ group to $(-\text{CHOH})$ group and $(-\text{COOH})$ group to (CH_2OH) , along with reacting at $(\text{C}=\text{C})$ bond to form alcohol (anti-Markovnikov's rule).



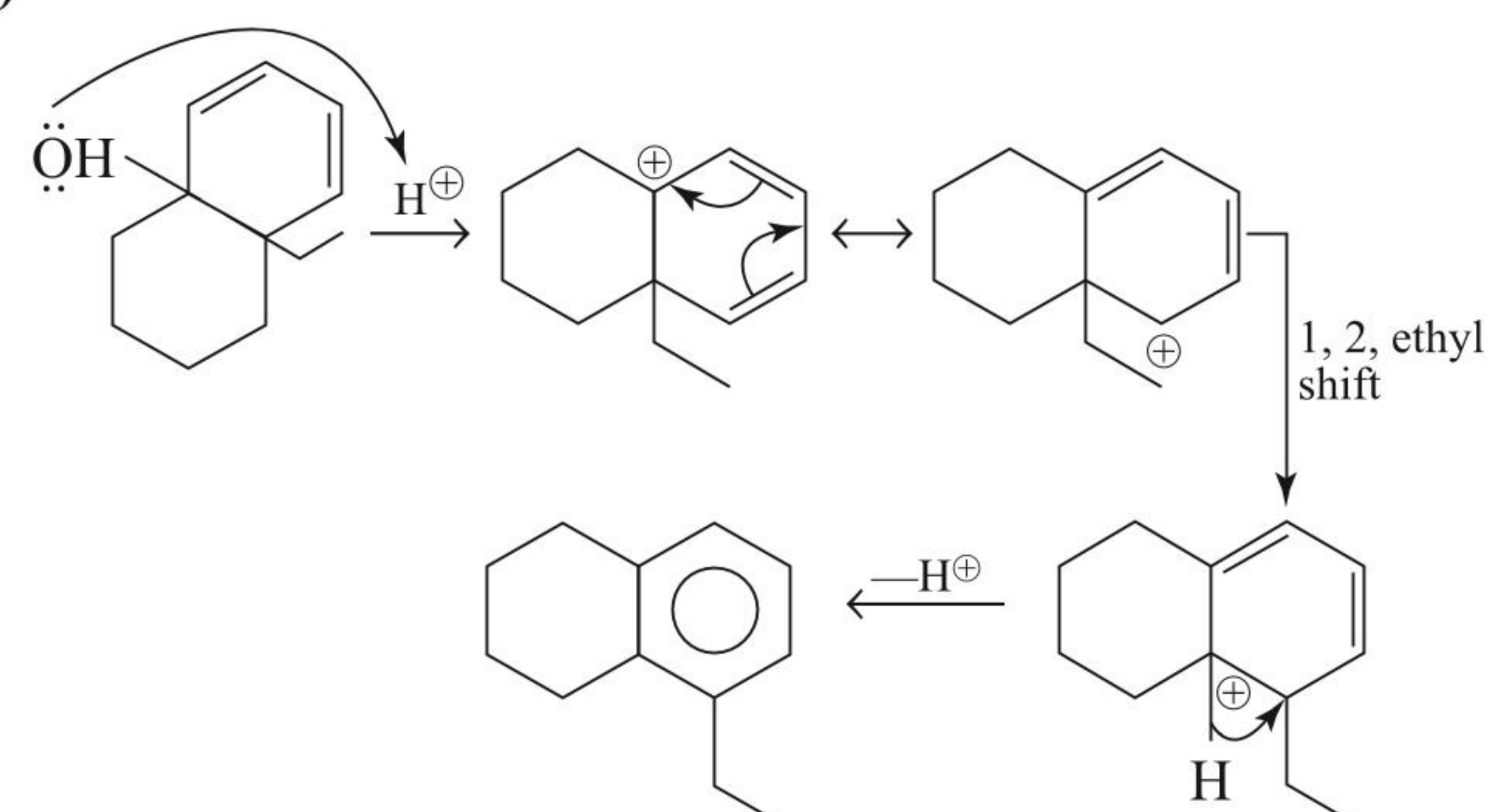
24. (3) $\text{B}_2\text{H}_6/\text{THF}$ besides reacting at $(\text{C}=\text{C})$ also selectively reduces only $(-\text{COOH})$ group to $(-\text{CH}_2\text{OH})$ group in cyclic ester.



25. (3)



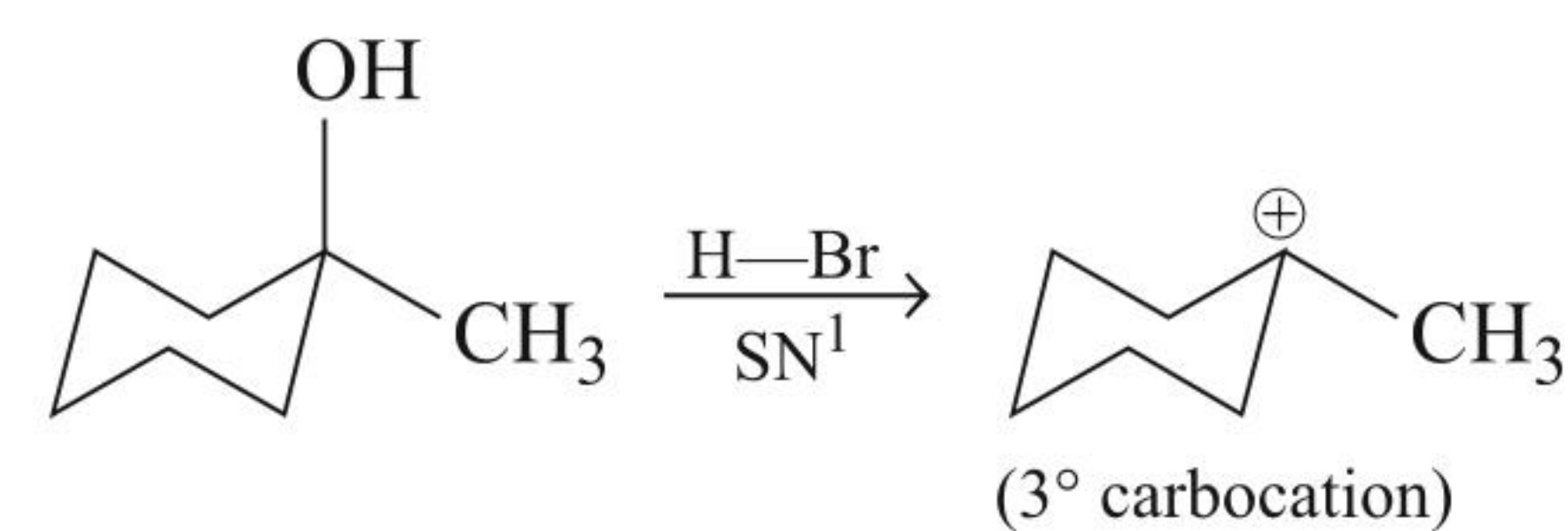
26. (1)



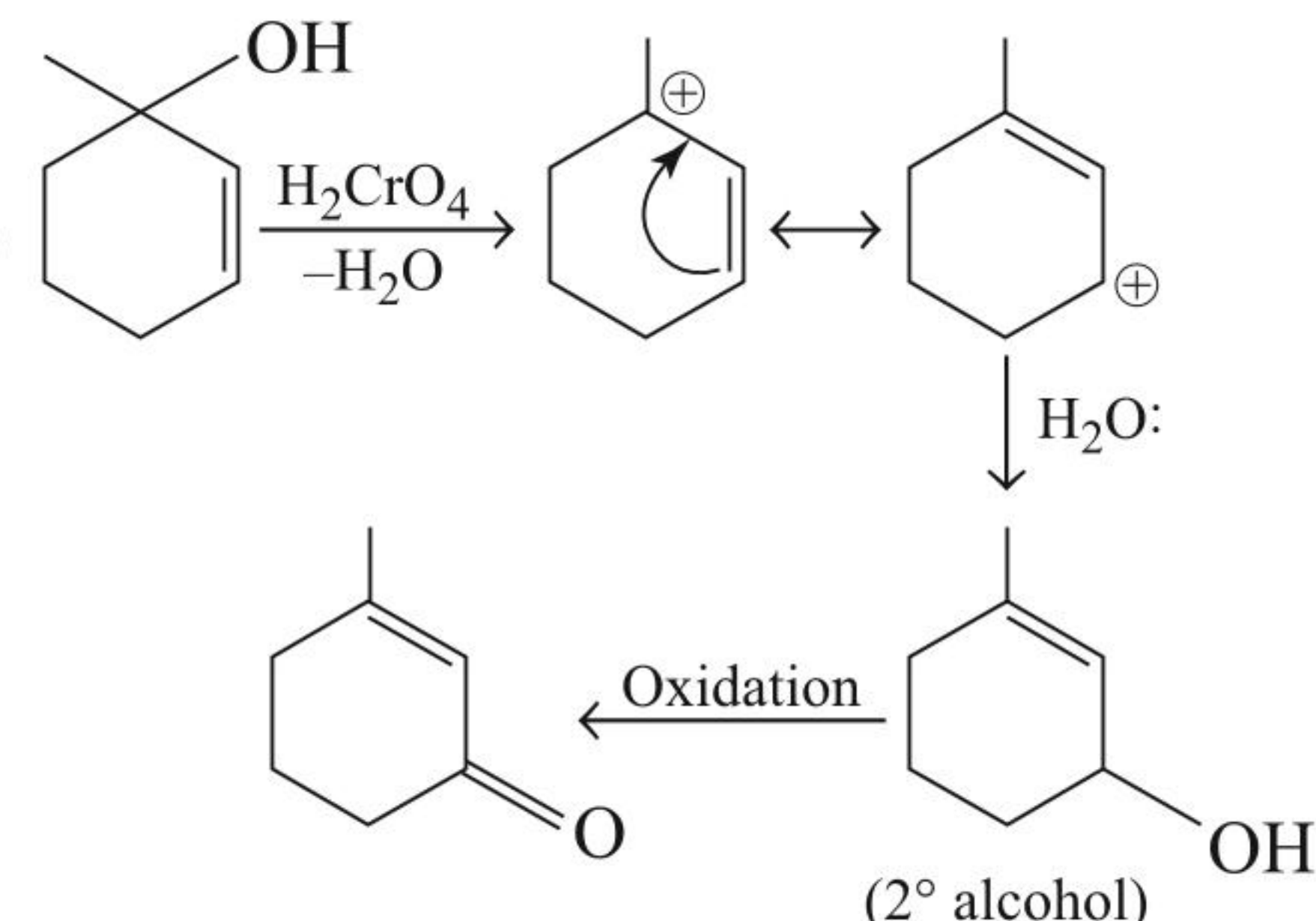
27. (2) More nucleophilic nitrogen will attack.

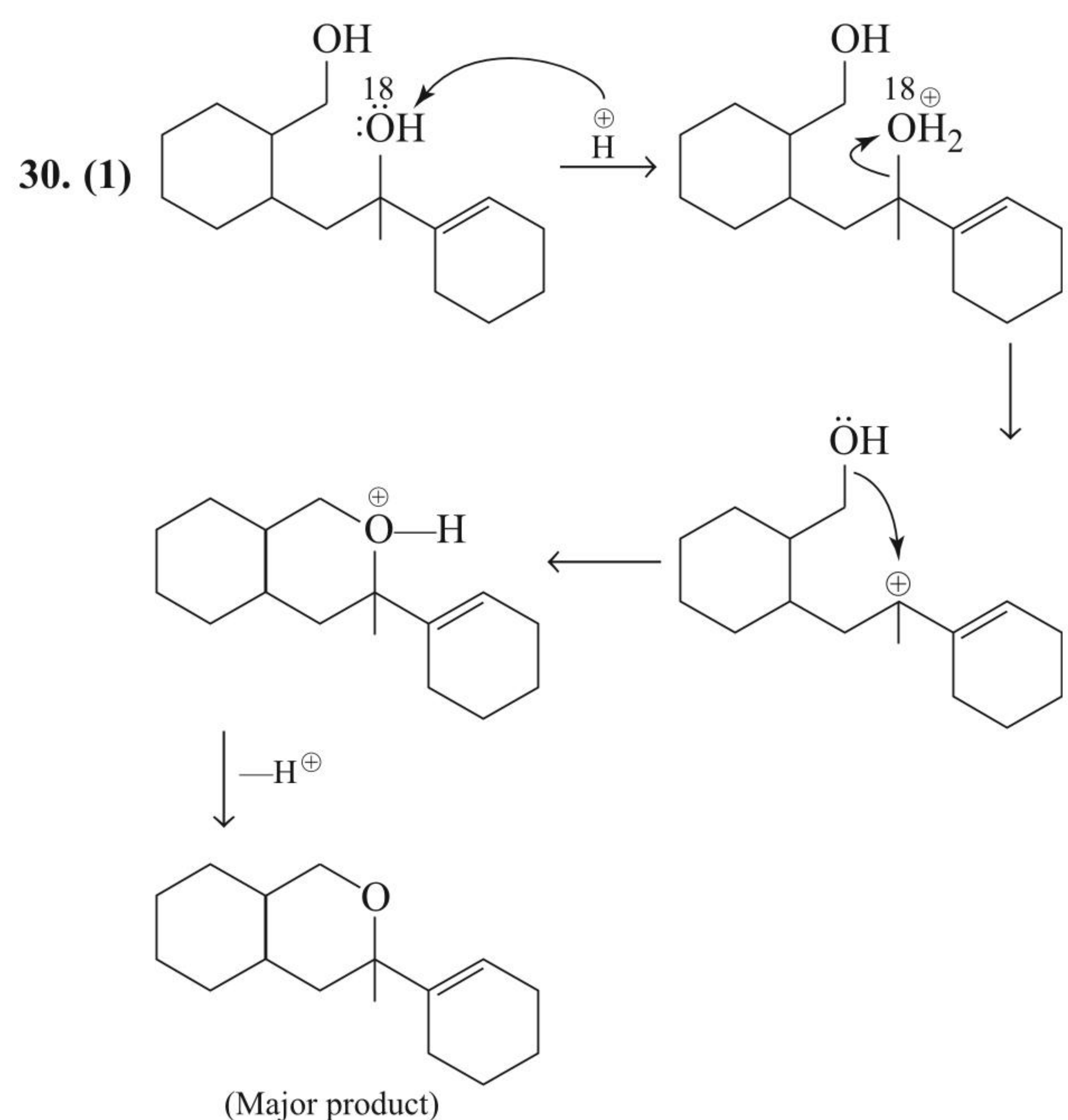
Acetylation at $(\text{N}-\text{H})$ occurs due to more ED power of $(-\text{NH})$ than $(-\text{OH})$ group

28. (2) 3° alcohol when reacts with HBr it gives $\text{S}_{\text{N}}1$ reaction.

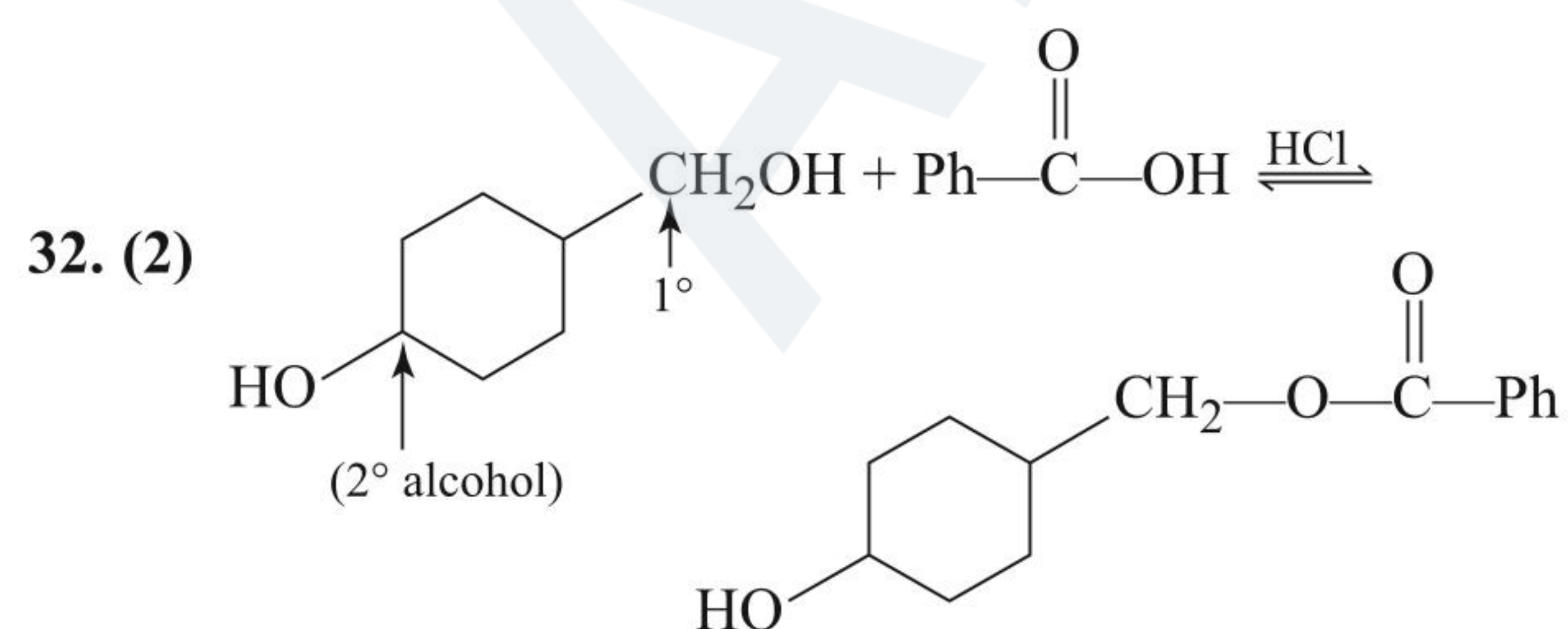
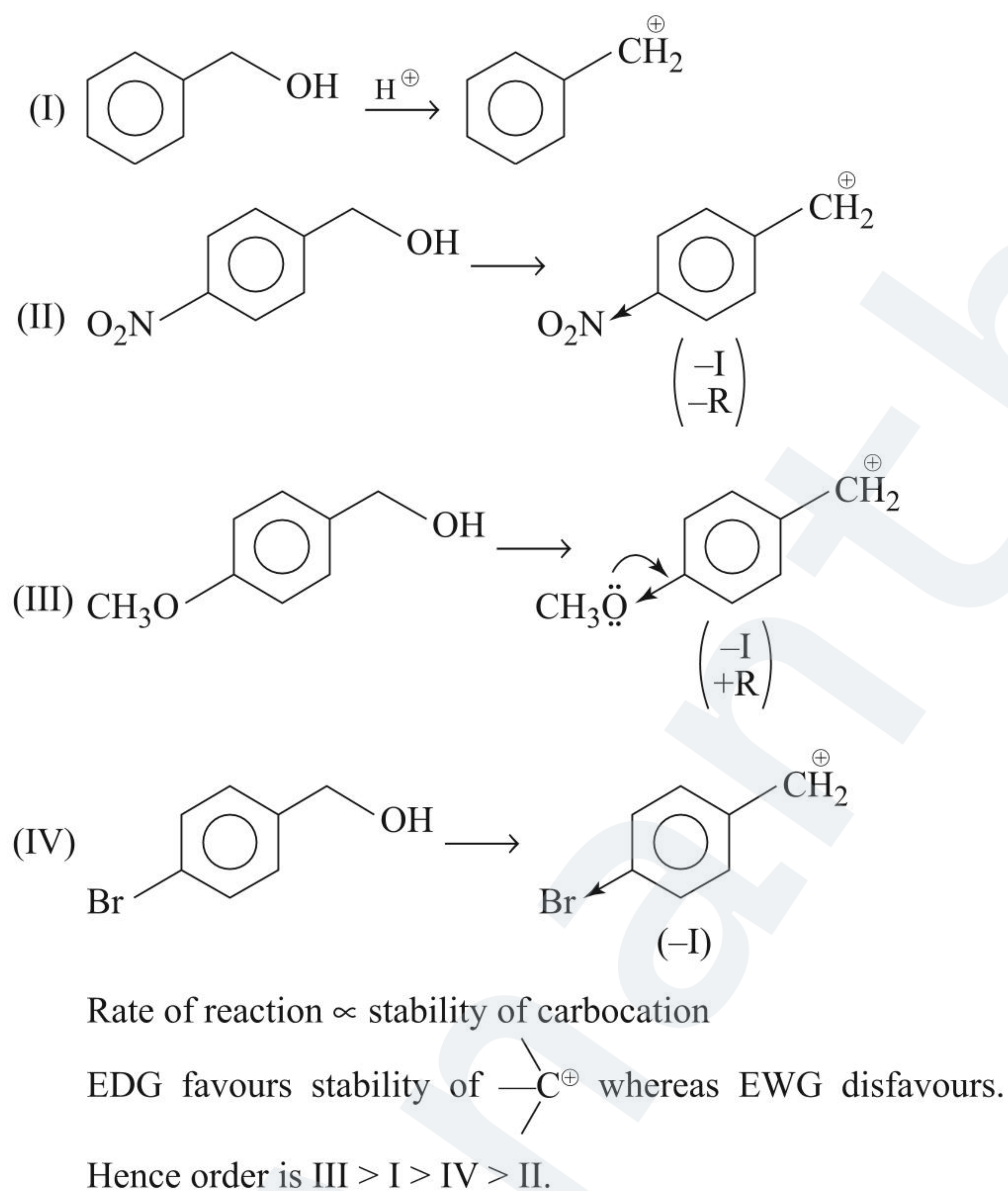


29. (2)

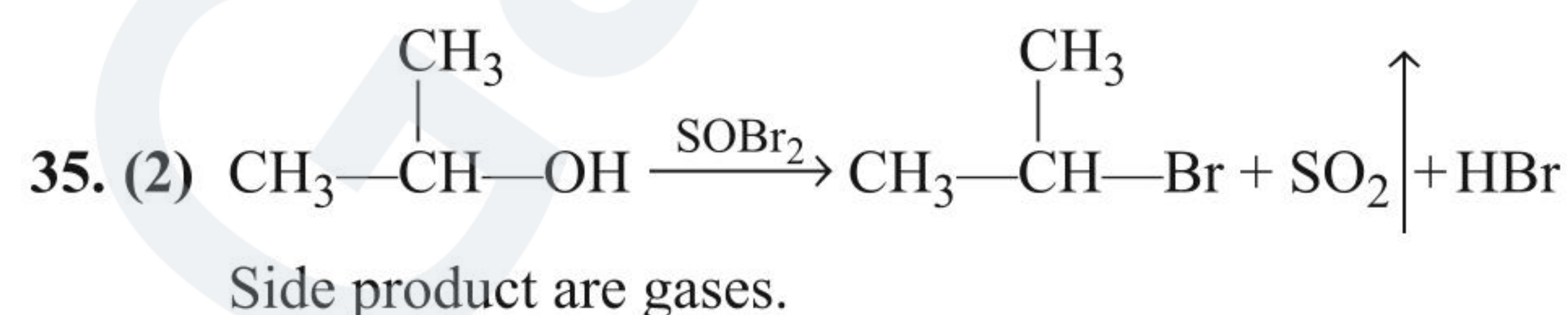
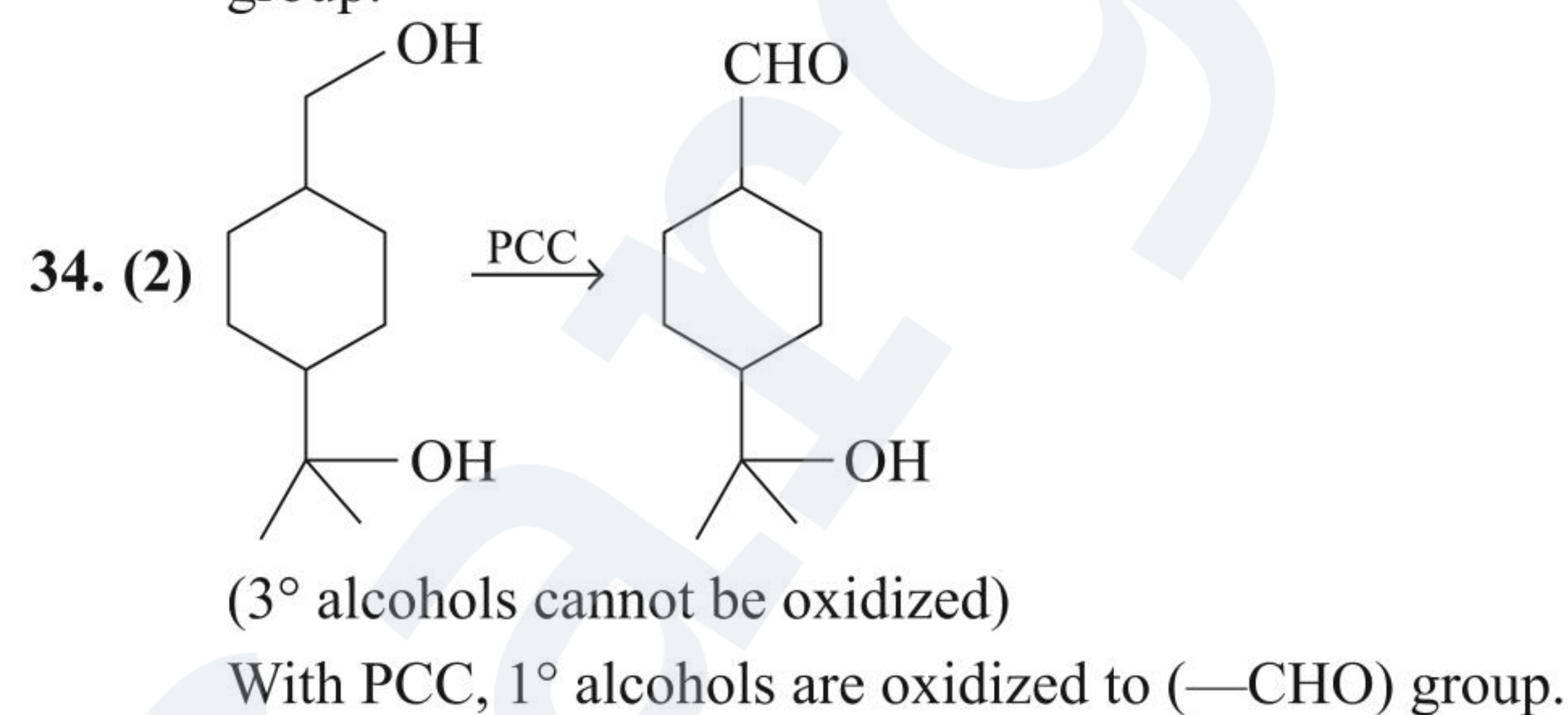
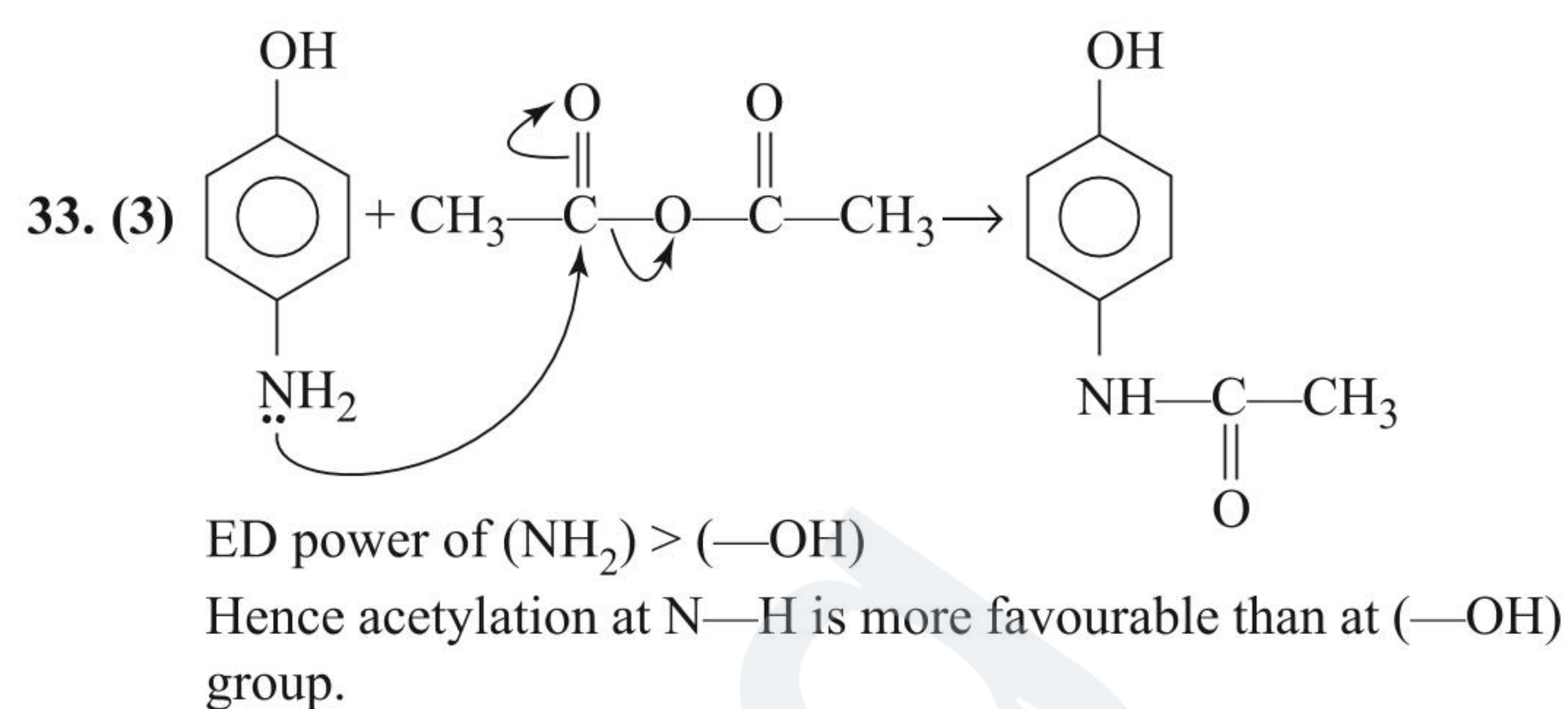




31. (1) More stable carbocation more is the rate towards HBr (acid).

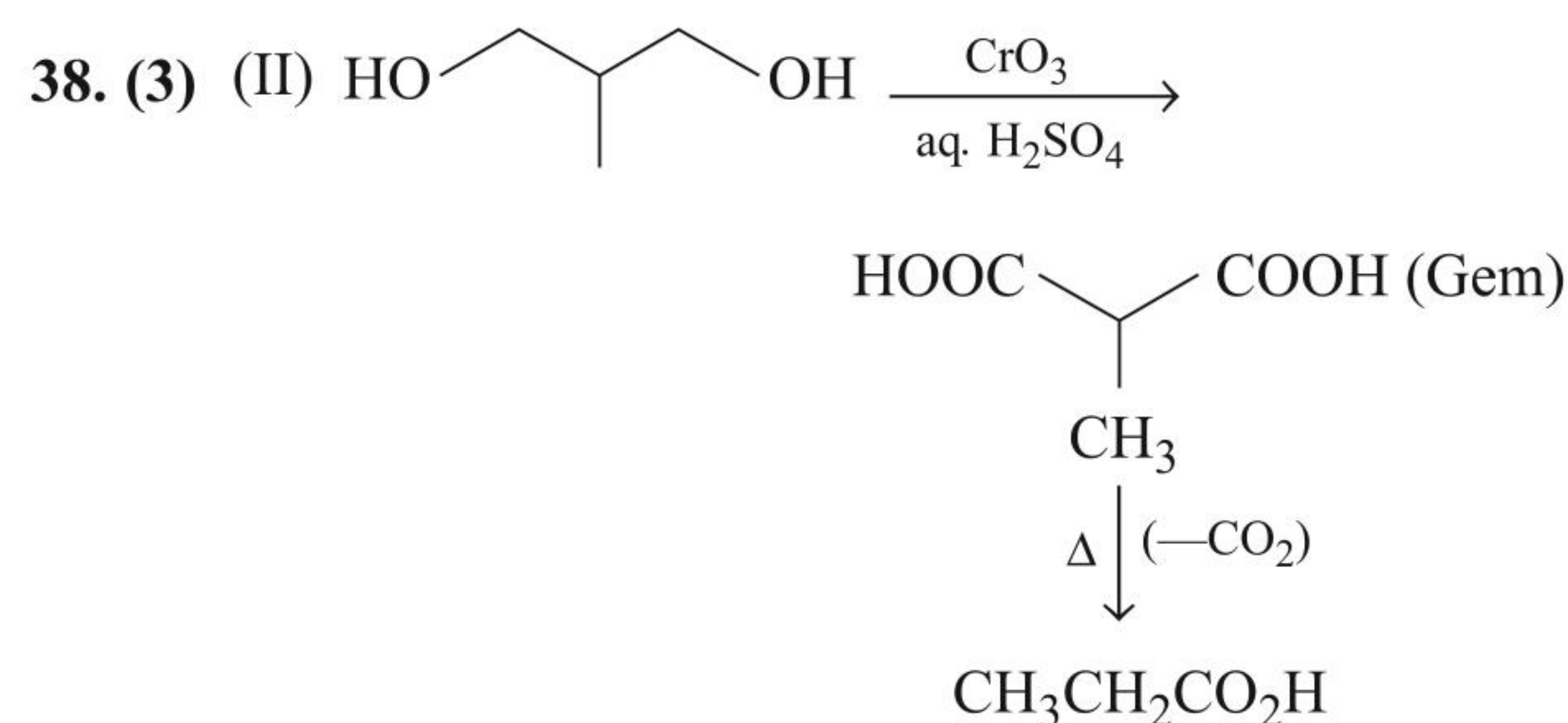
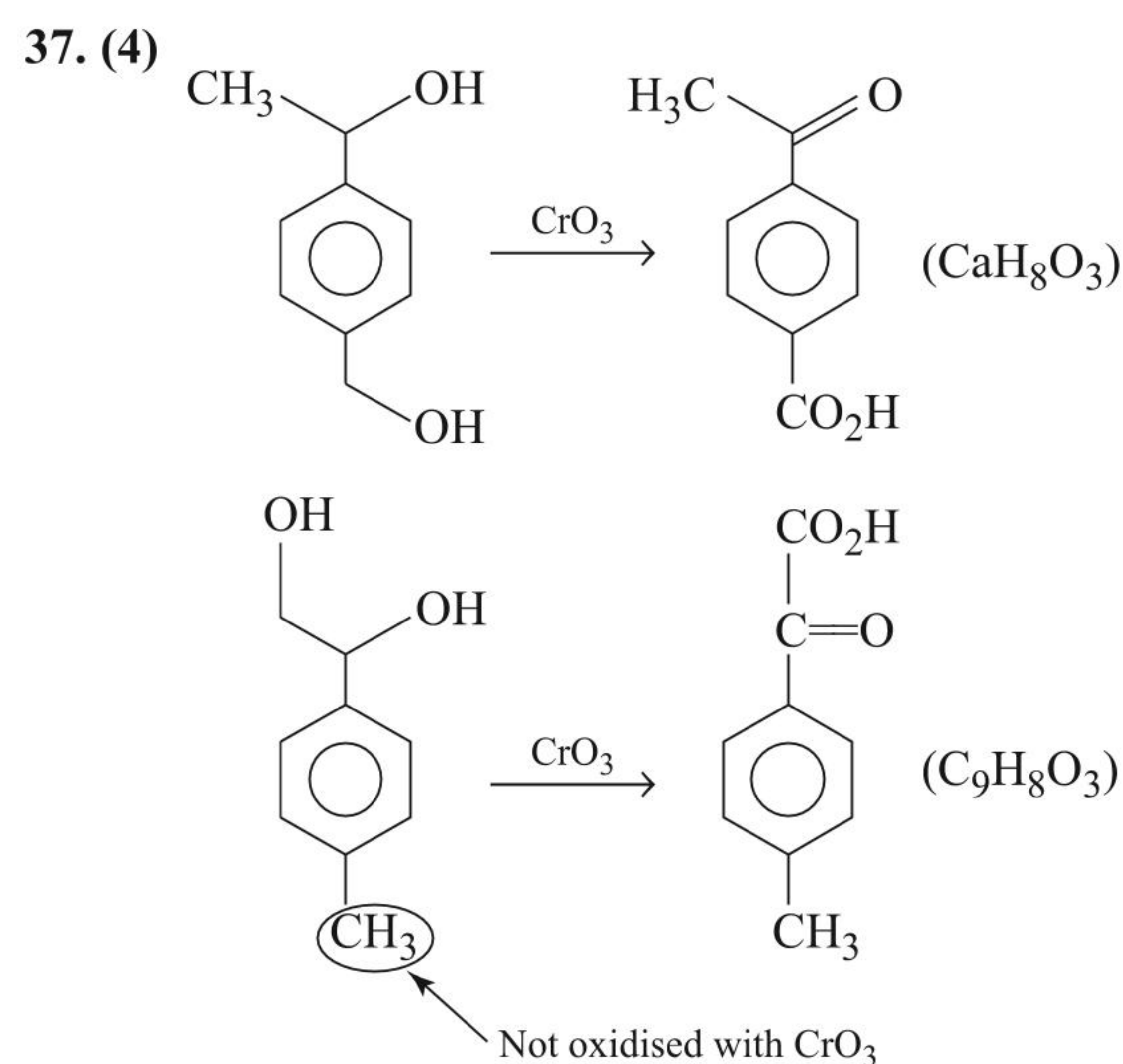
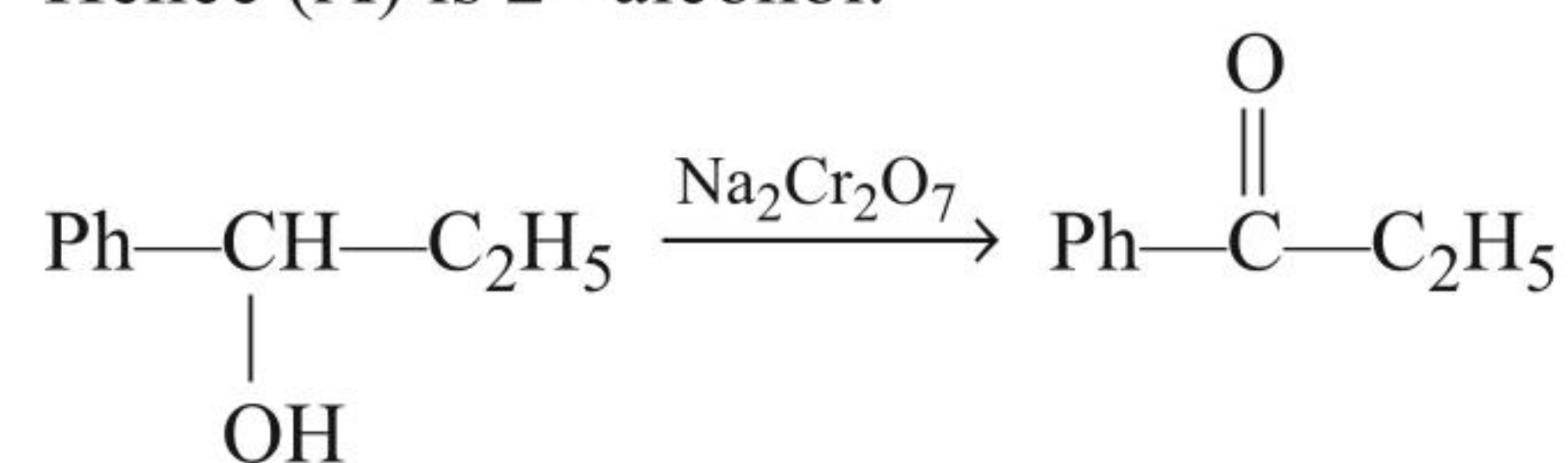


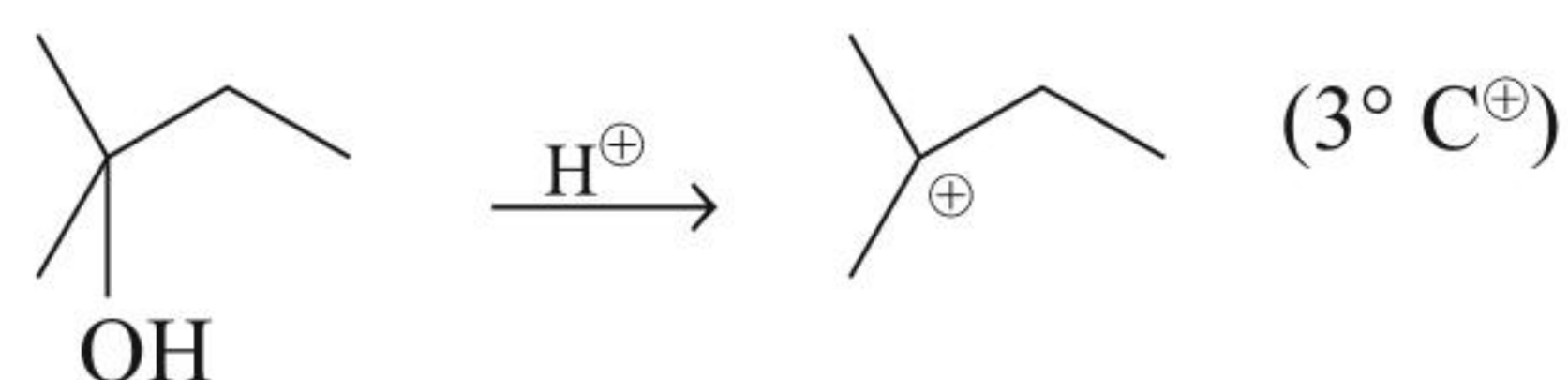
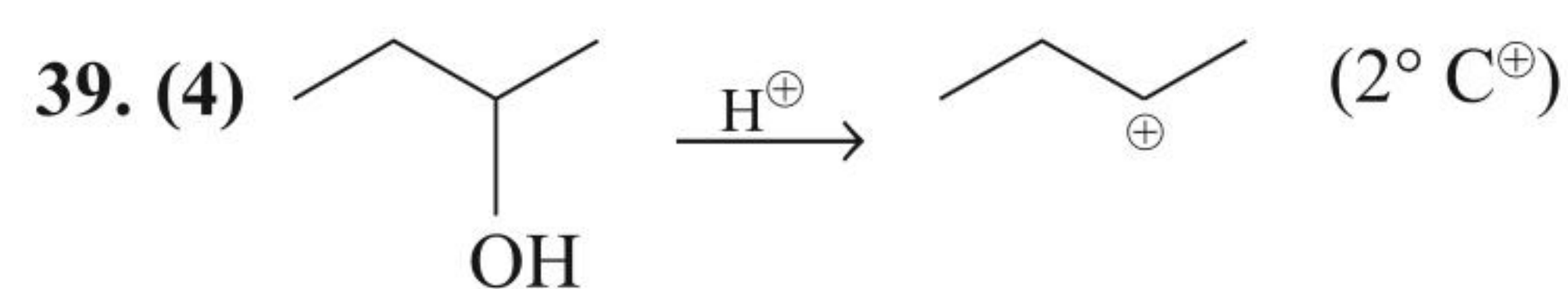
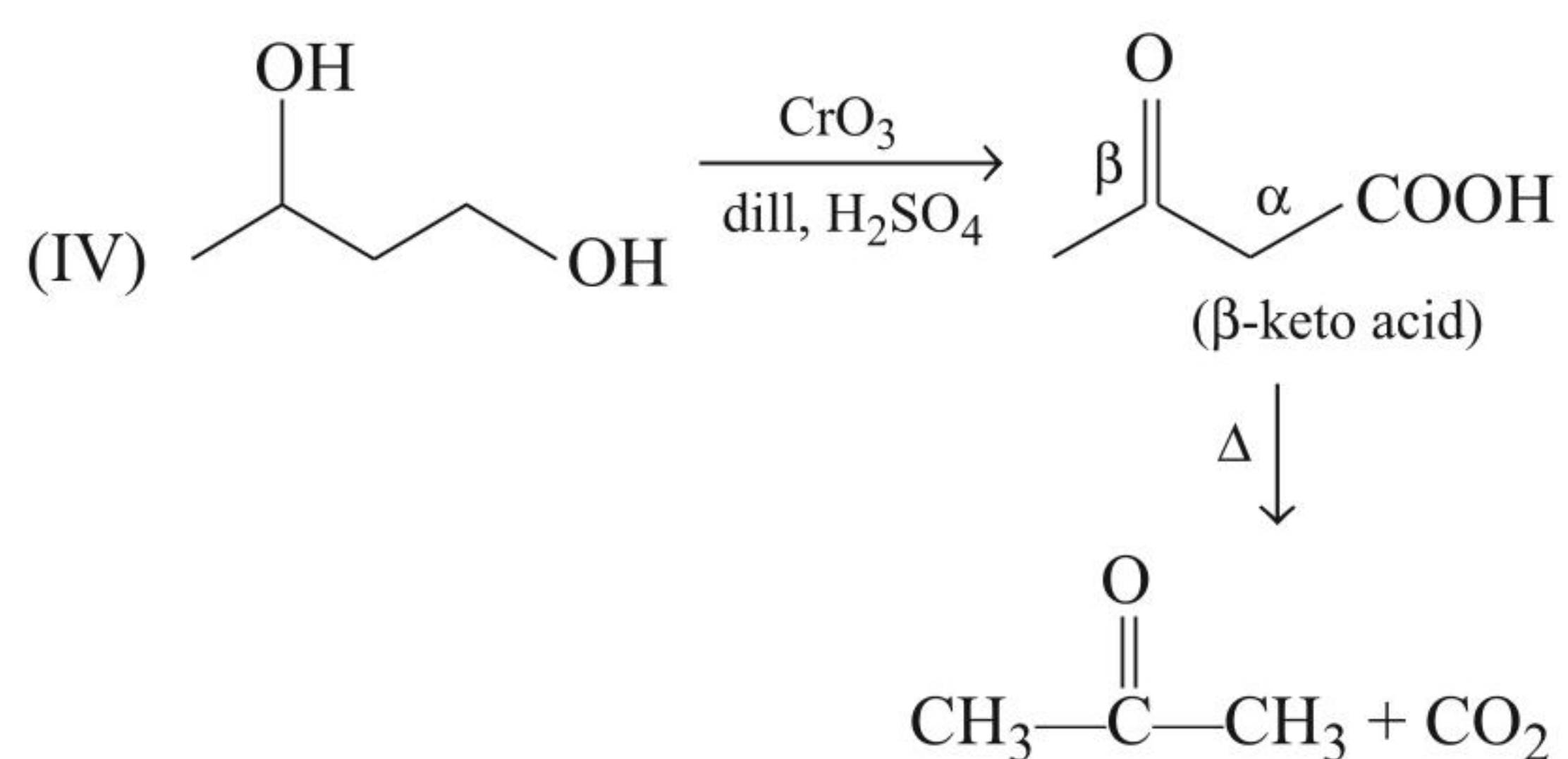
Order of nucleophilicity in esterification is
 $1^\circ > 2^\circ > 3^\circ$ alcohol (due to steric hindrance)



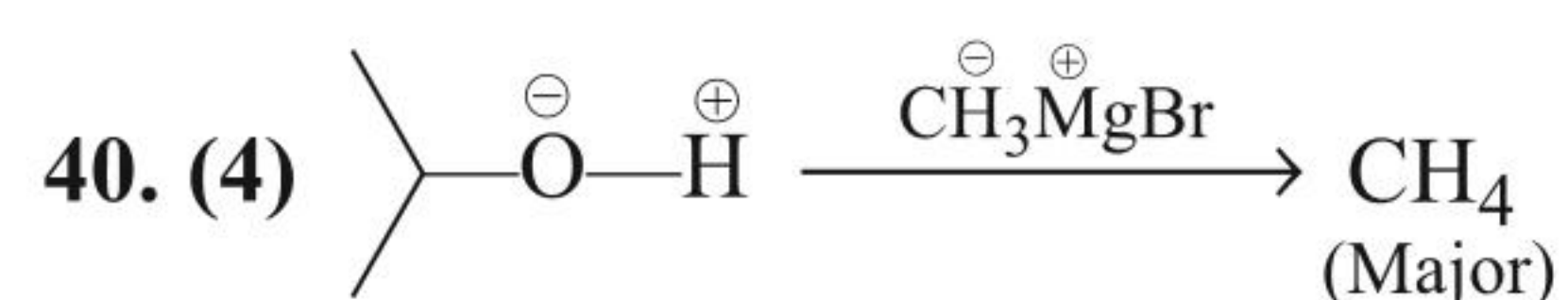
36. (2) DU in A = 4°, (benzene ring)

DU in B = 5° (benzene ring and C=O group)
 Hence (A) is 2°-alcohol.





Stability order of carbocation $3^\circ > 2^\circ$

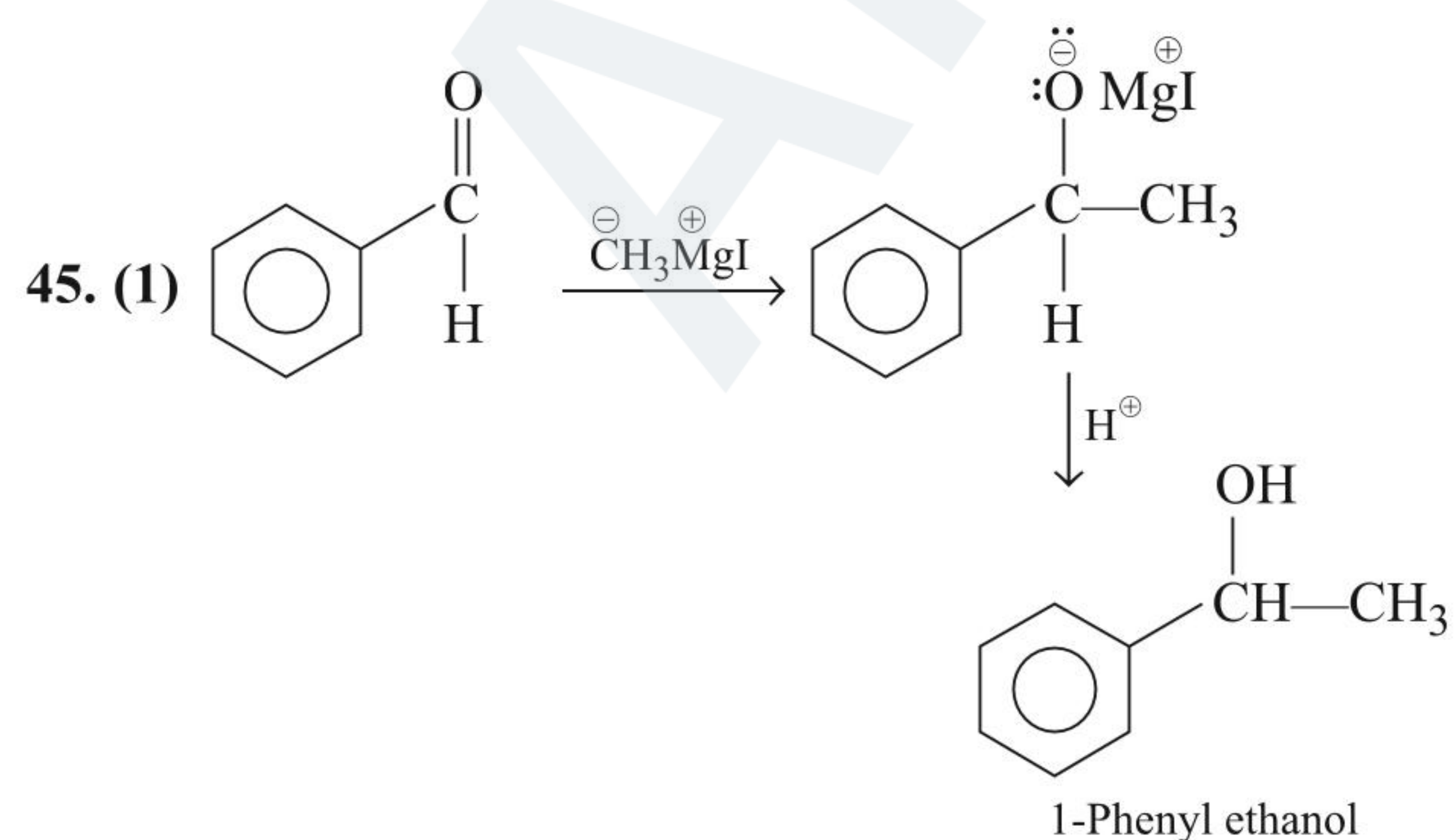
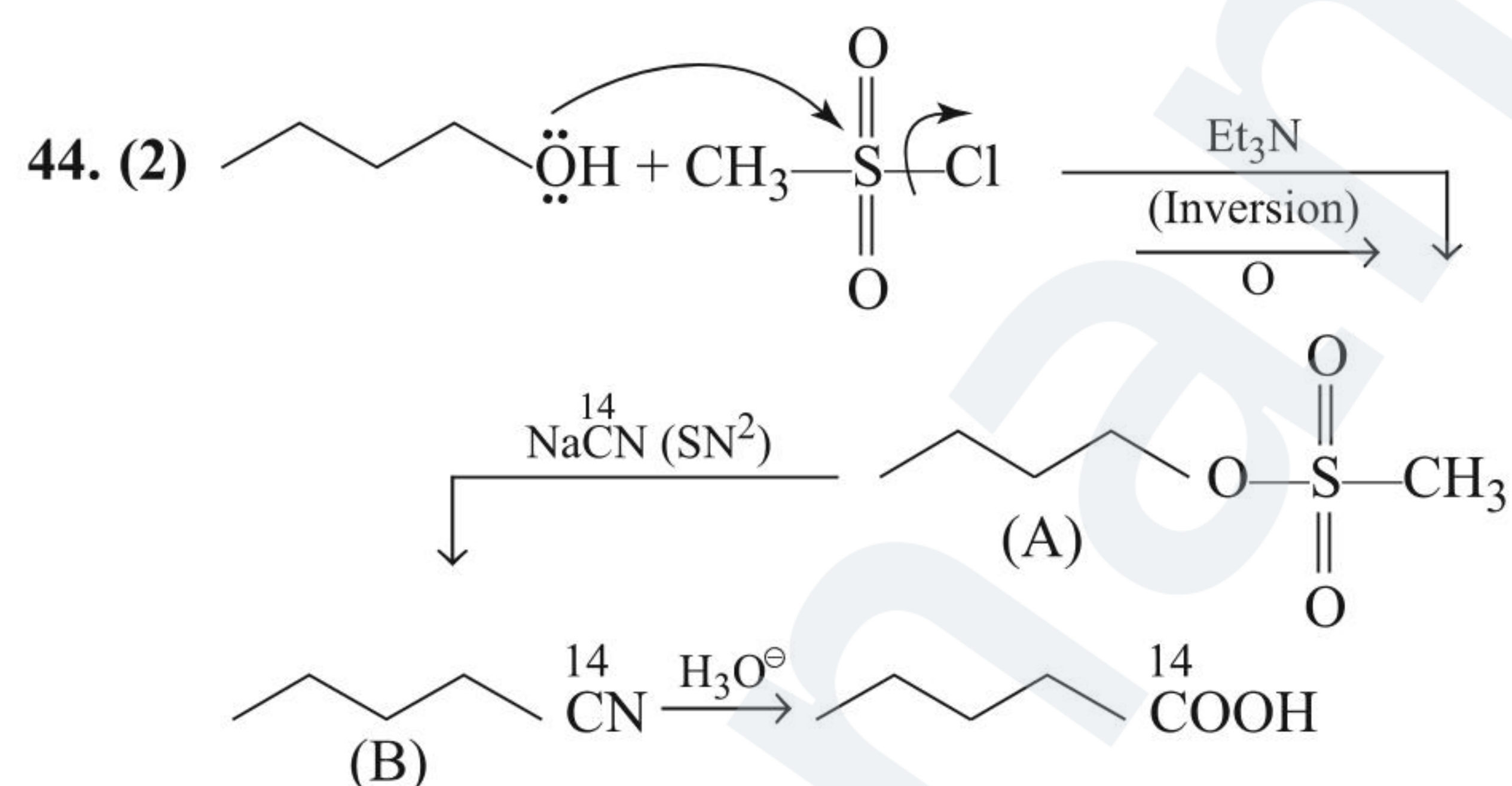
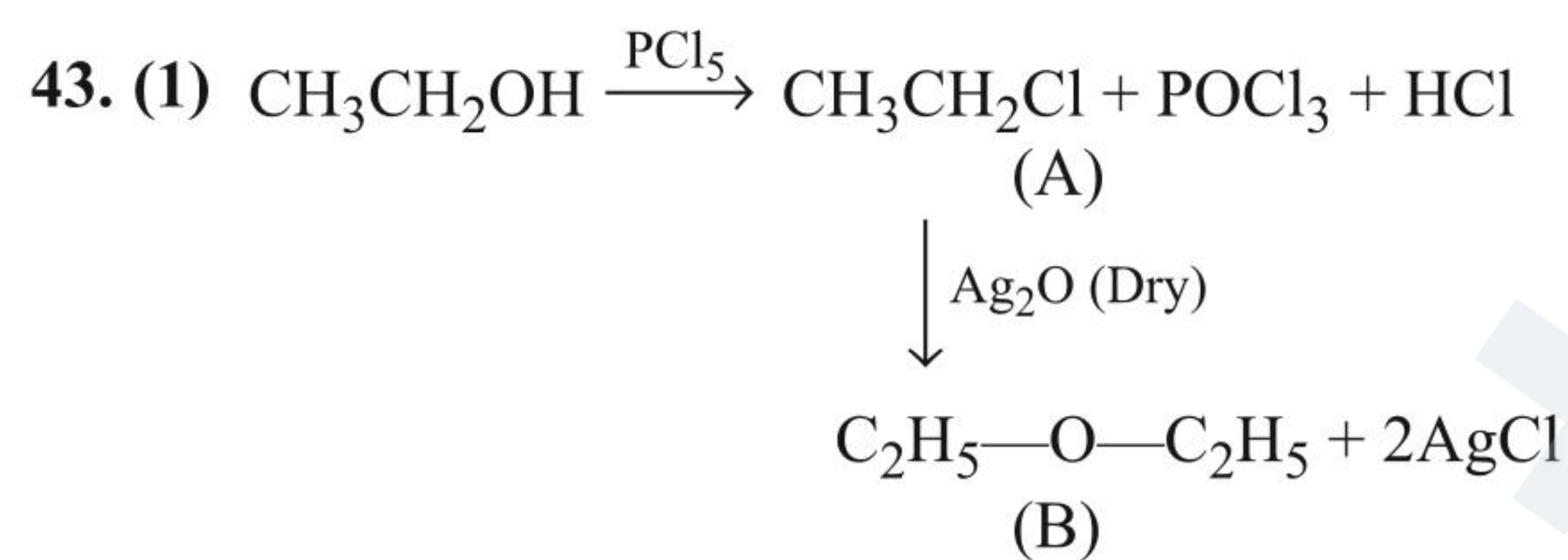


Acid-base reaction occurs

41. (4) Factual

42. (1) Alcohol shows acidic behaviour in esterification, so CH_3OH is most acidic among all the options, so rate of esterification will be maximum.

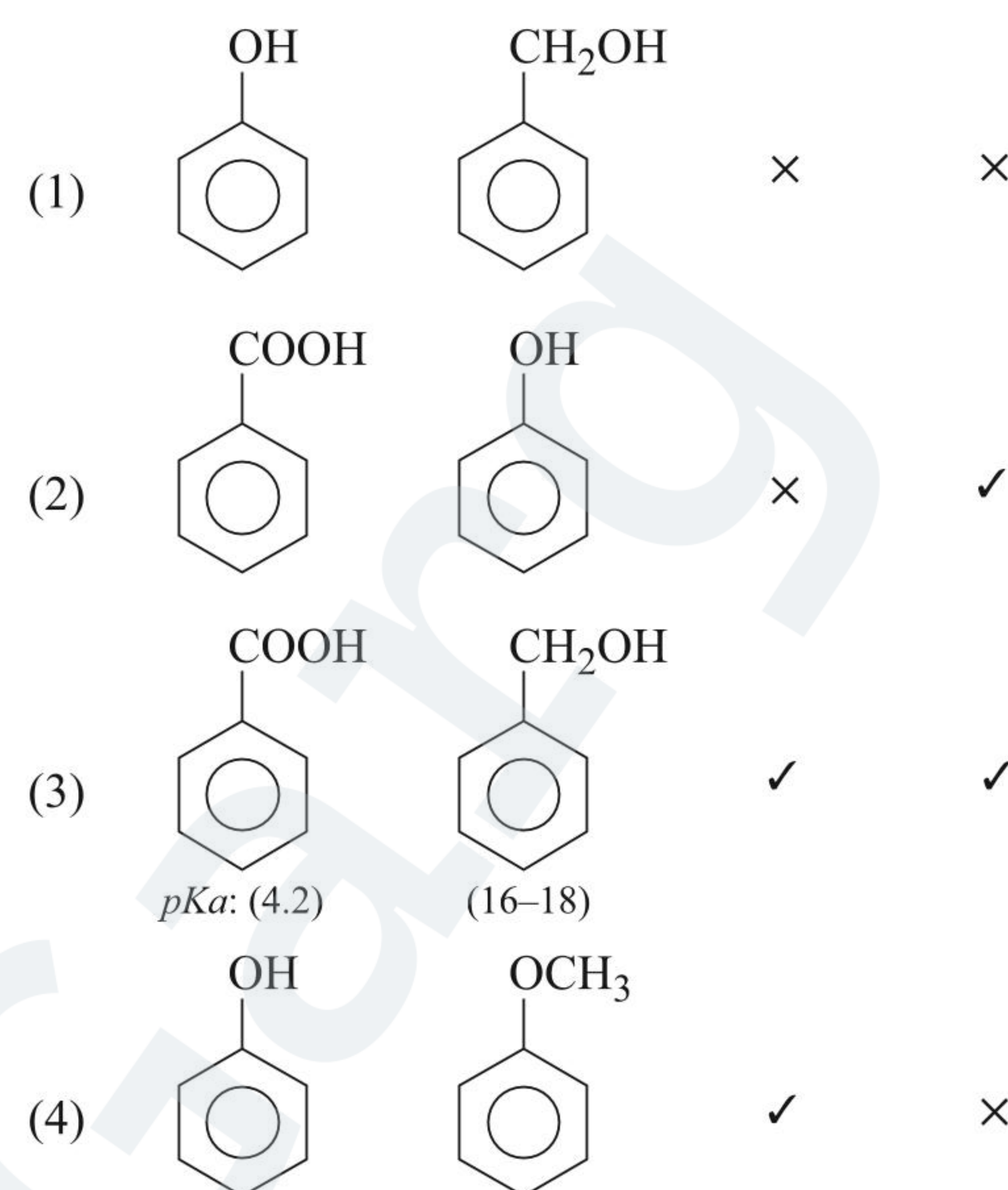
Less EDG (or less steric hindered) faster is the rate of esterification.



46. (3) For a compound to give positive NaHCO_3 test it must be more acidic than H_2CO_3 ($\text{pK}_a = 6.4$)

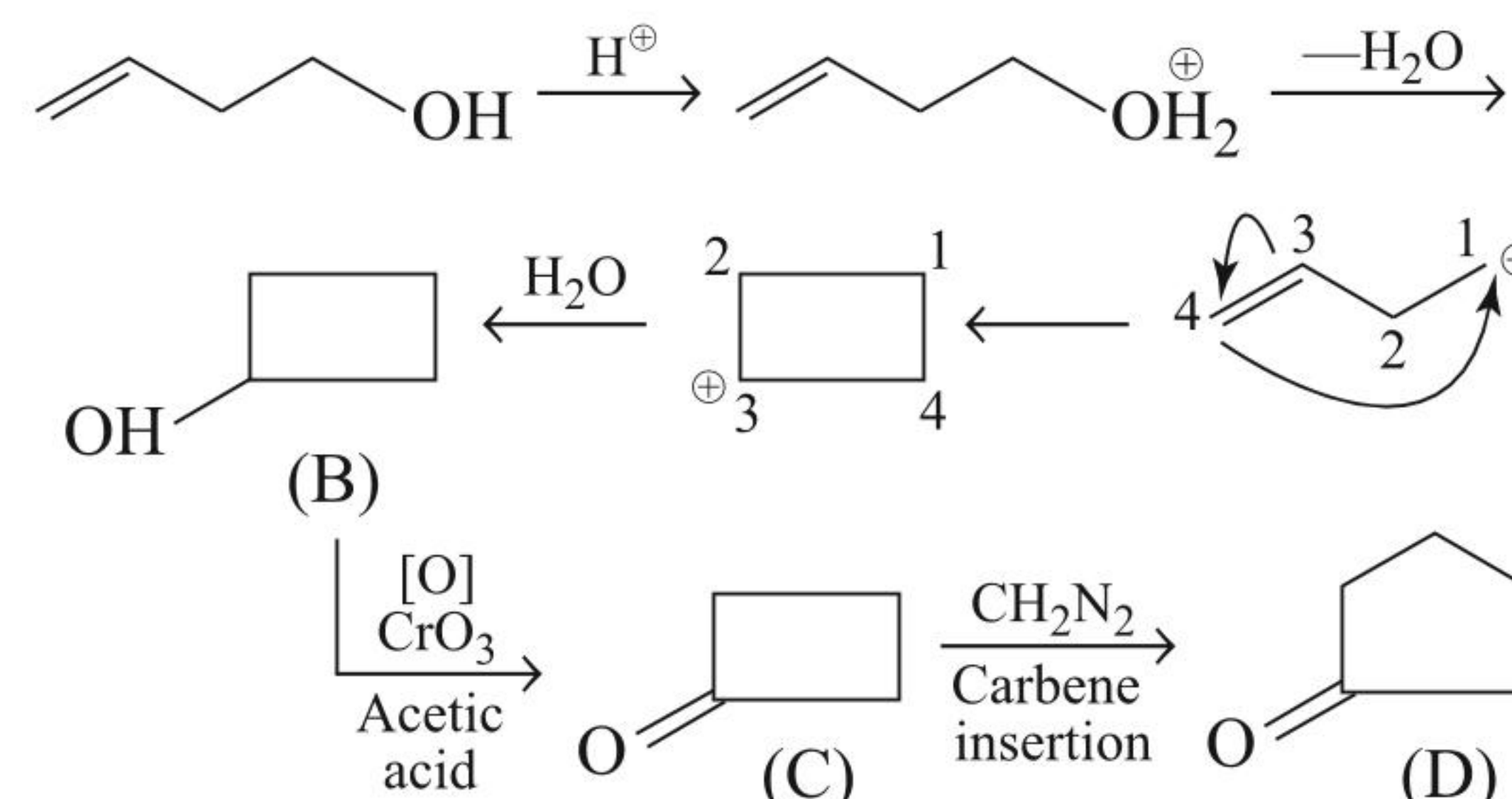
And for a compound to give positive NaOH test, it must be more acidic than H_2O ($\text{pK}_a = 15.7$)

NaOH NaHCO_3

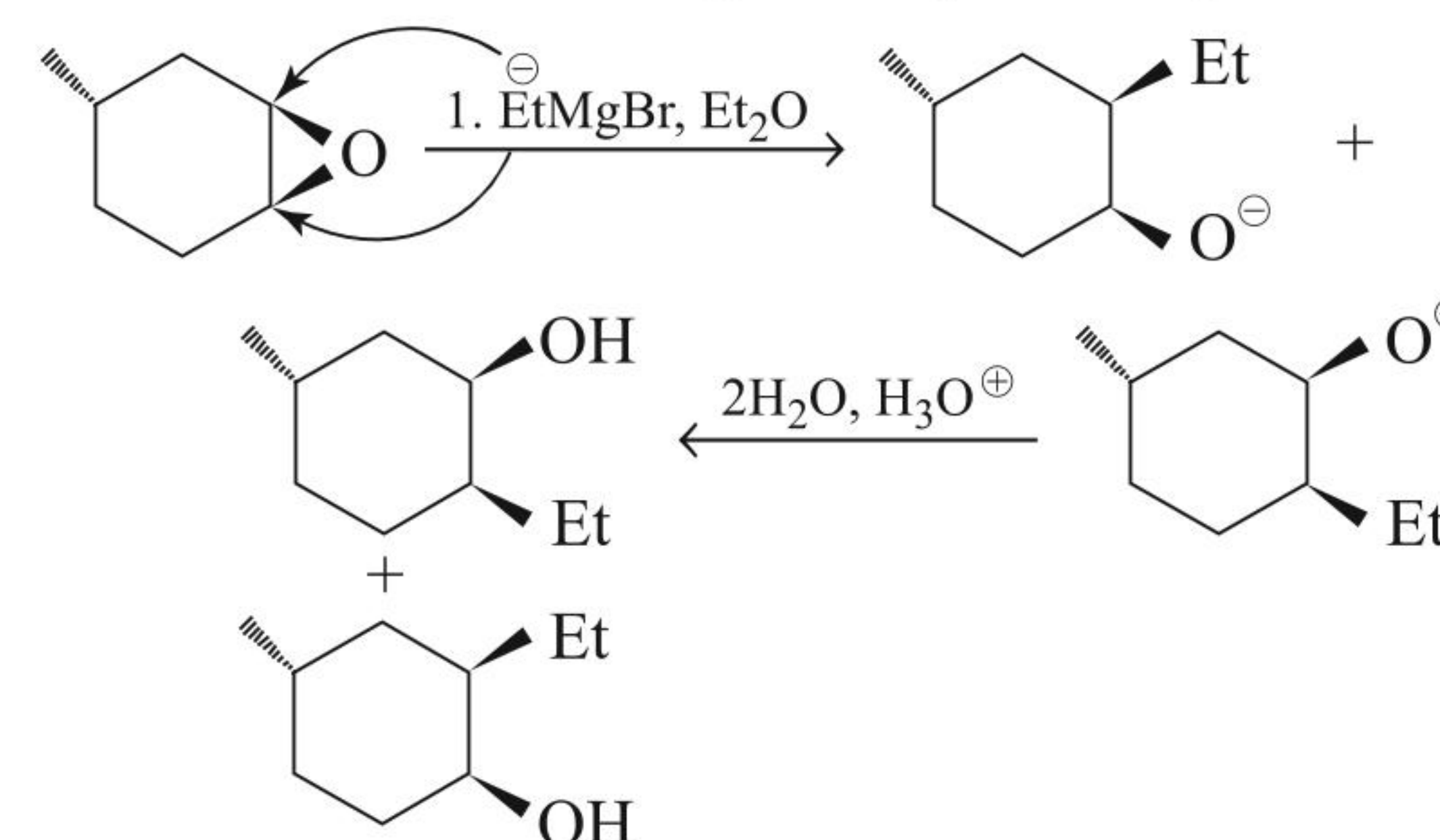


47. (2) Factual

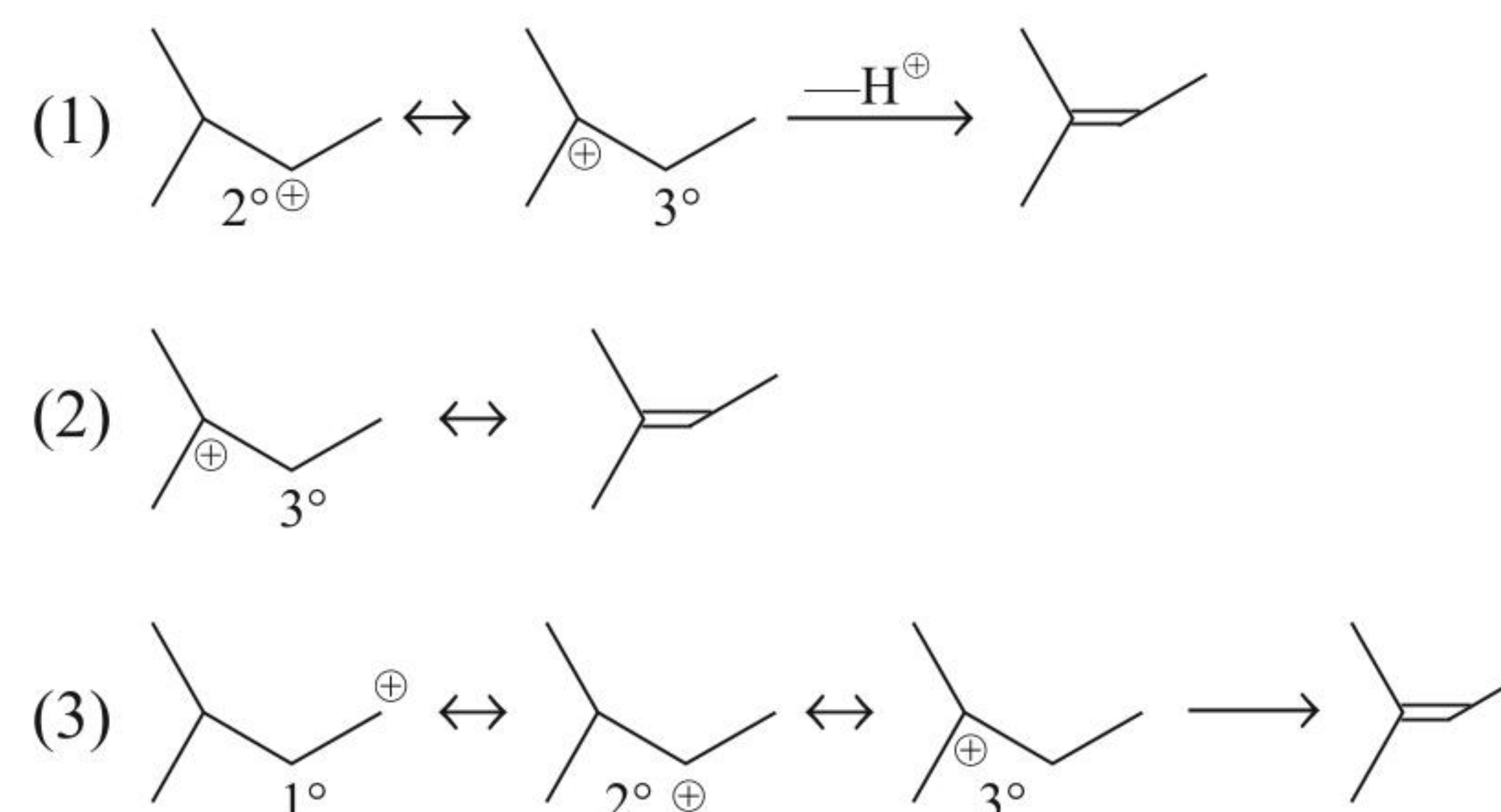
48. (1) DU in (A) = 1°. (A) is unsaturated alcohol.



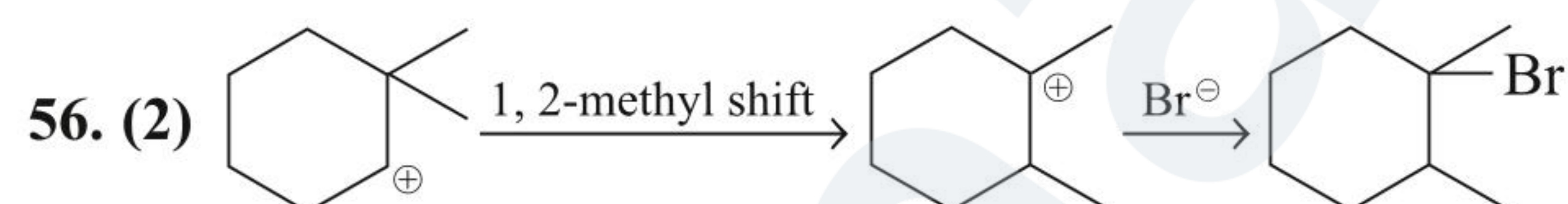
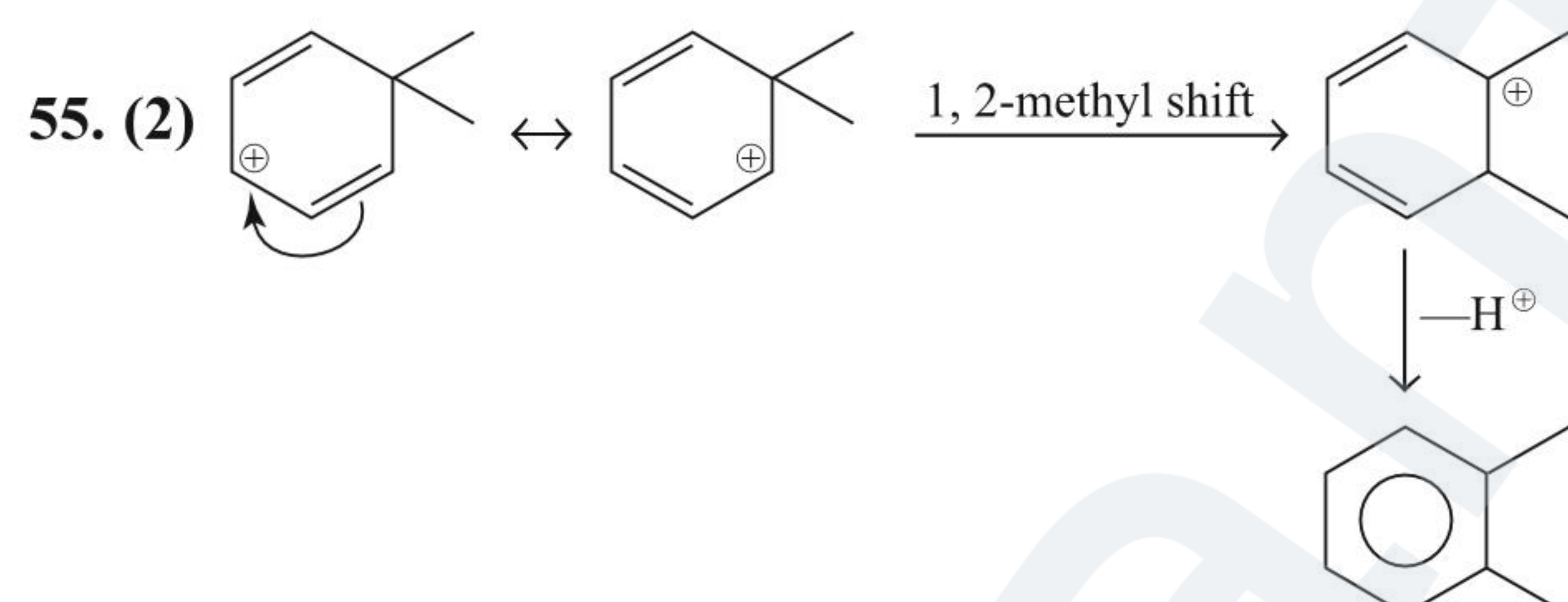
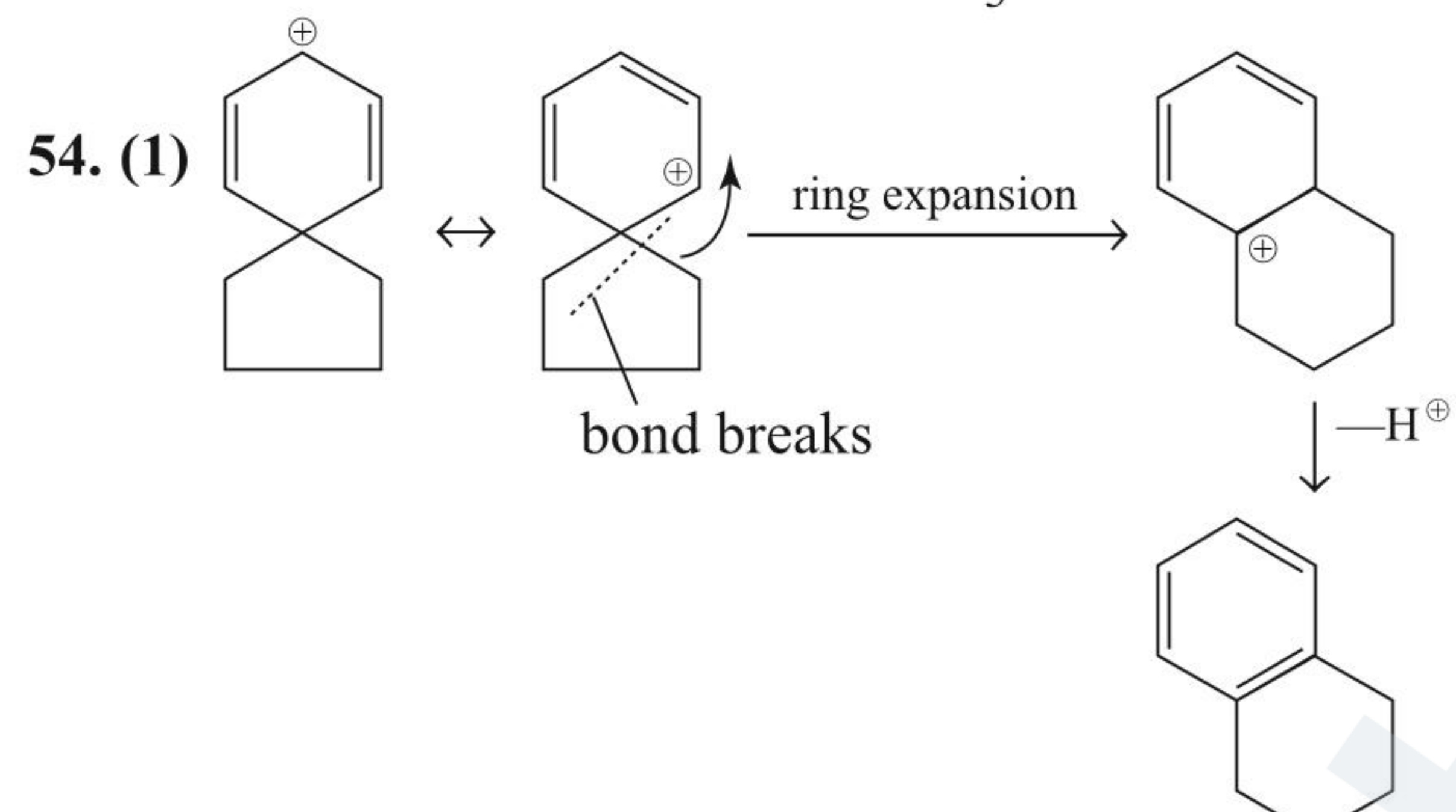
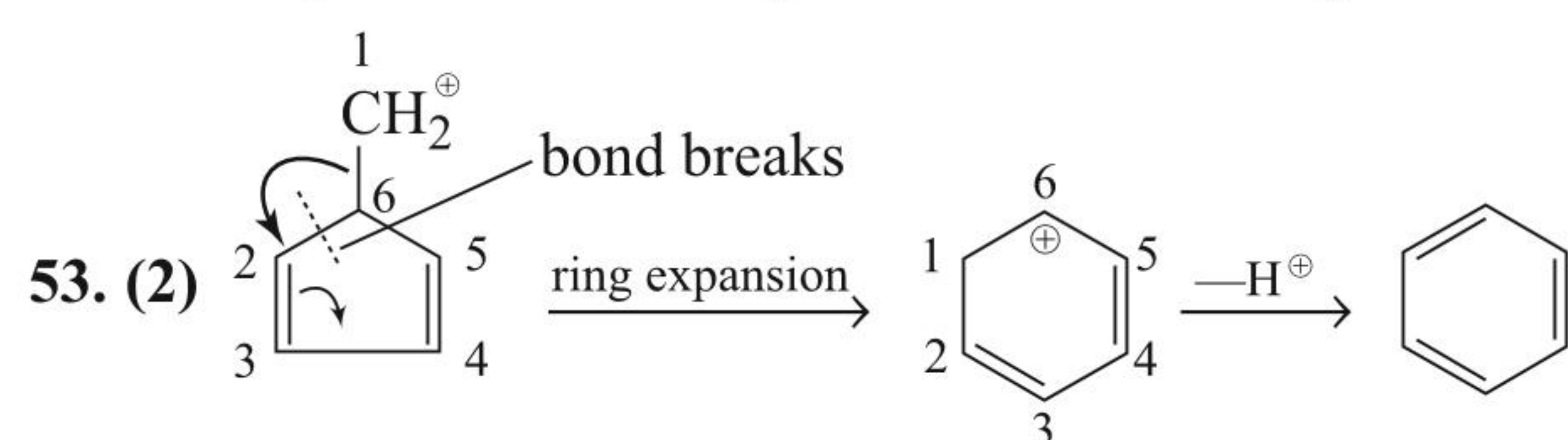
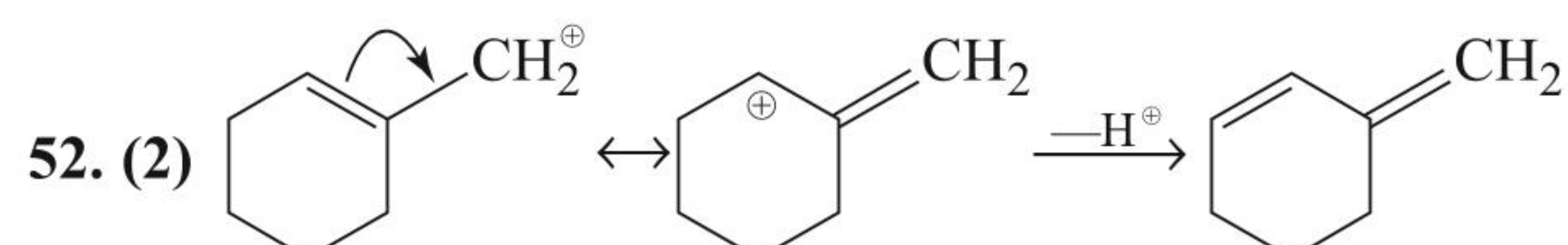
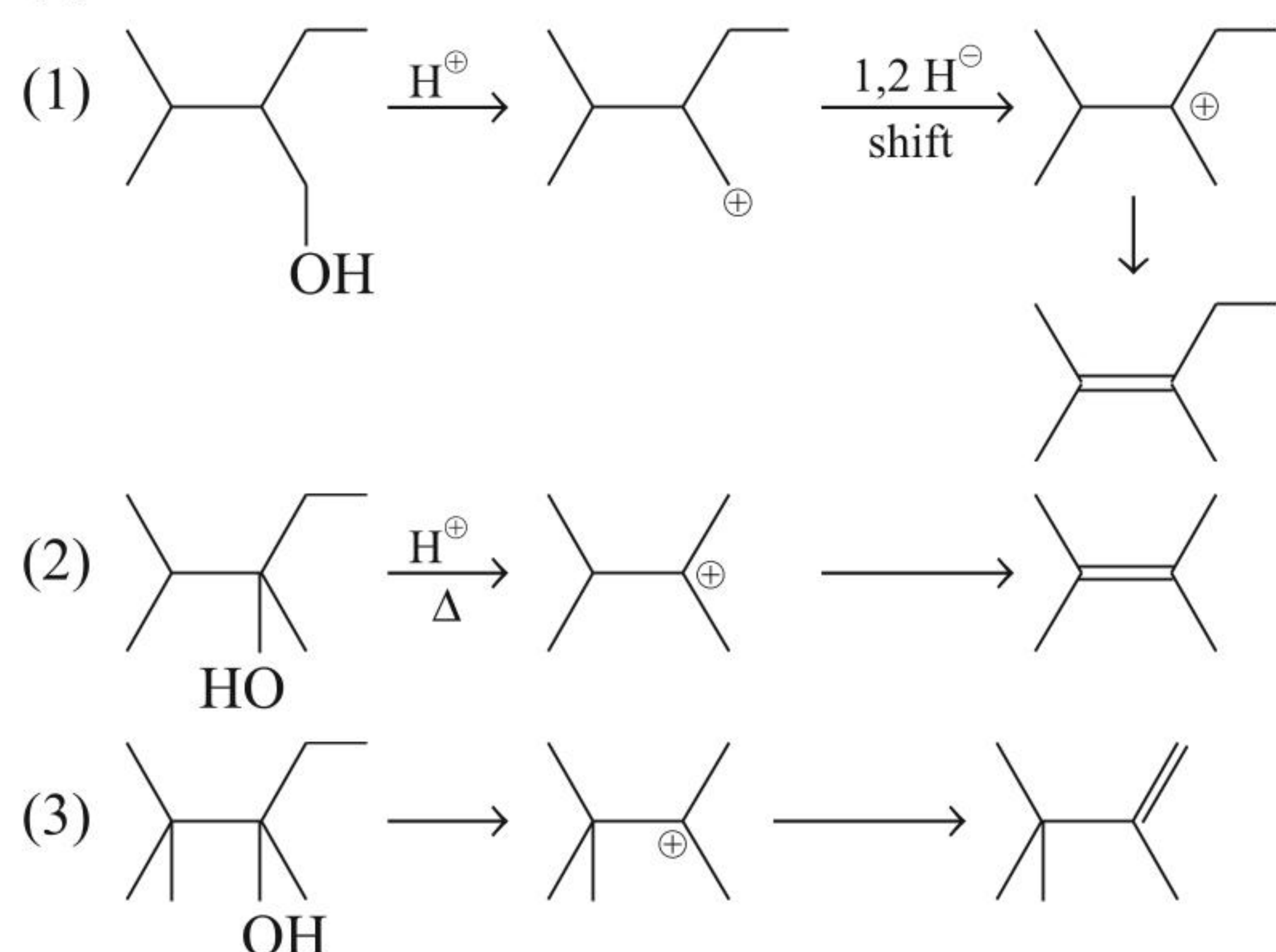
49. (1) Both sides attack of EtMgBr on epoxide is possible



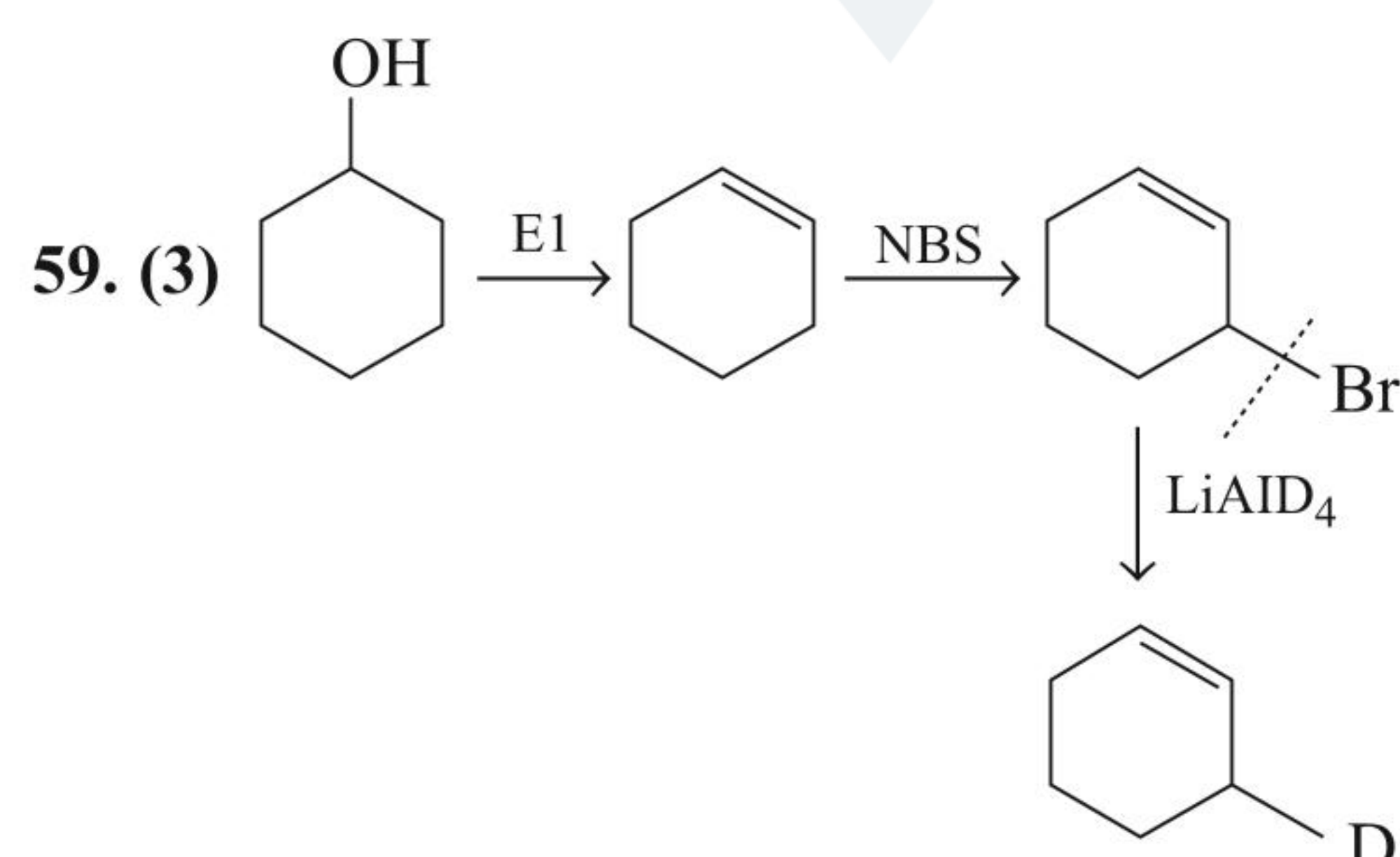
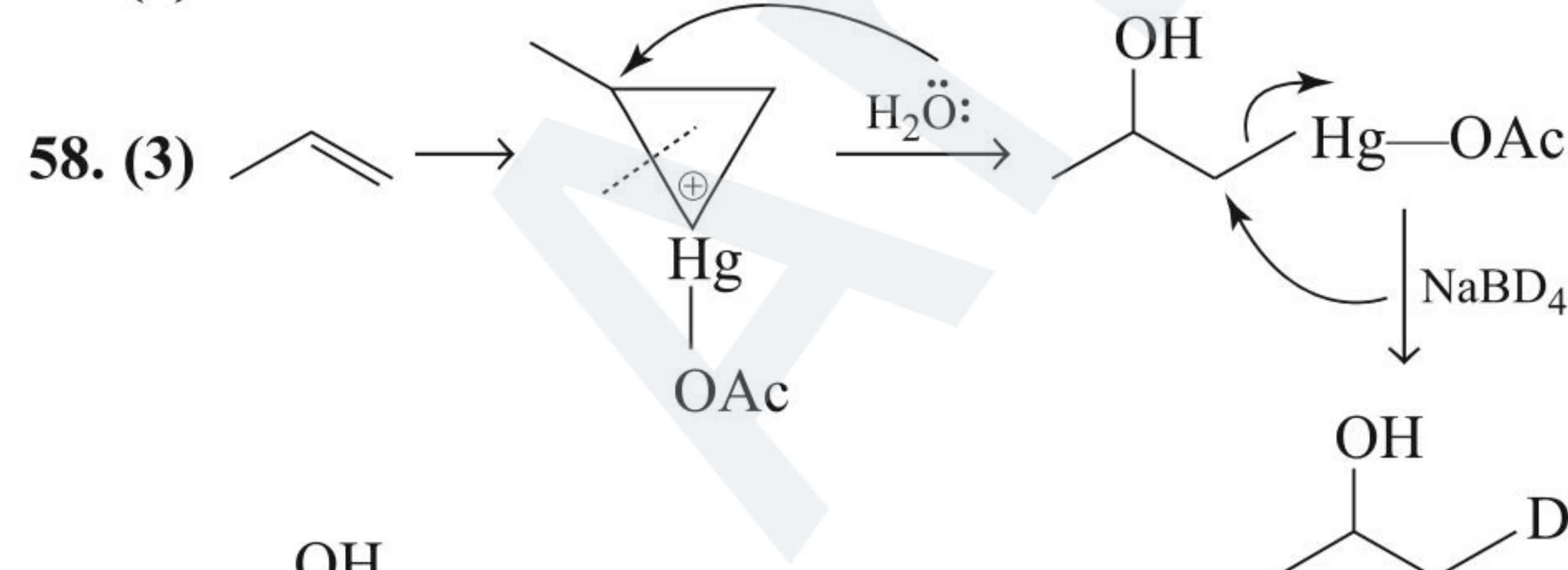
50. (4) (1), (2), (3) all give same carbocation as an intermediate.



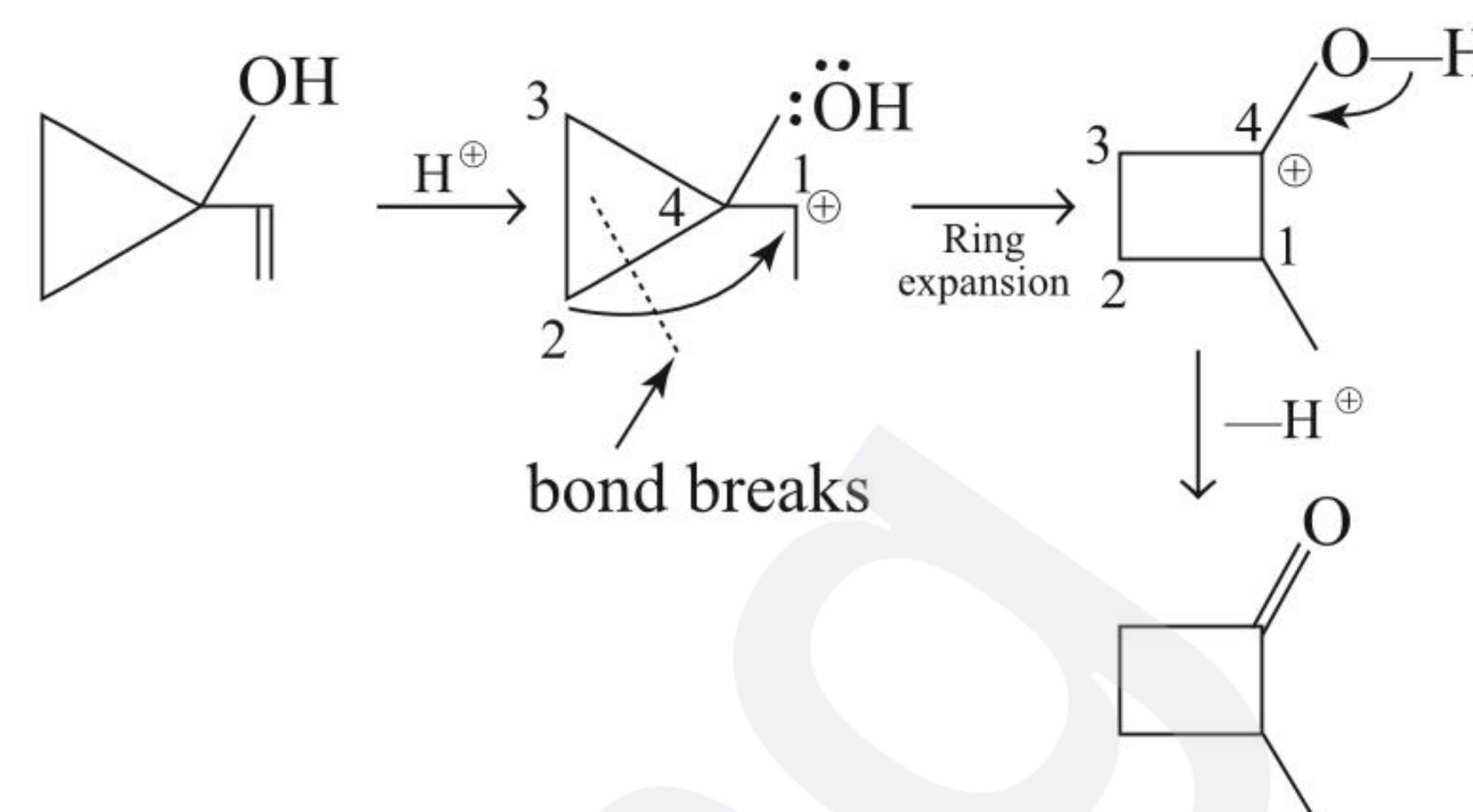
51. (2)



57. (1) Factual



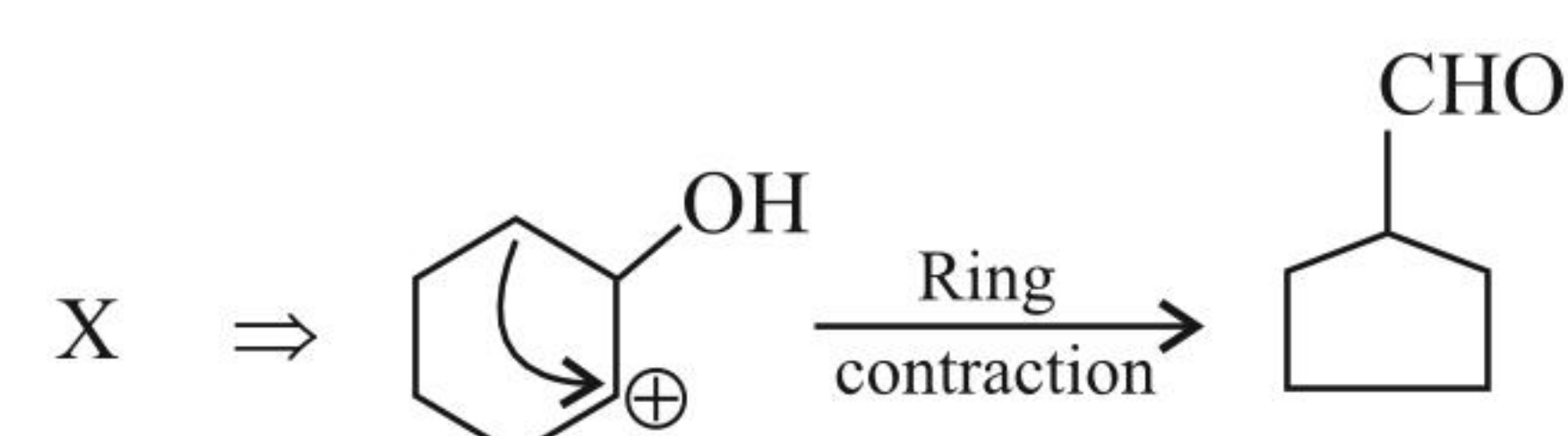
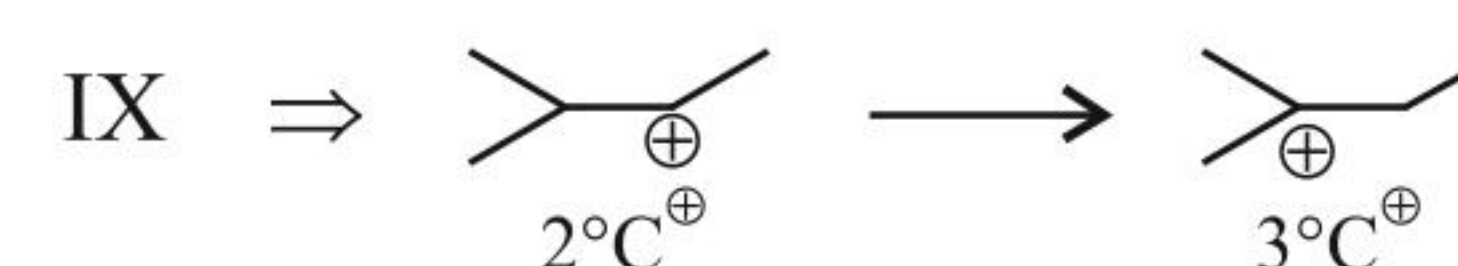
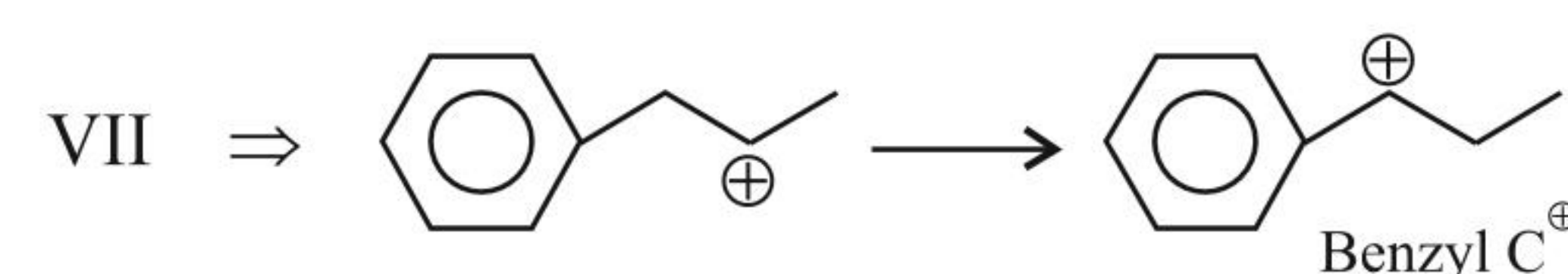
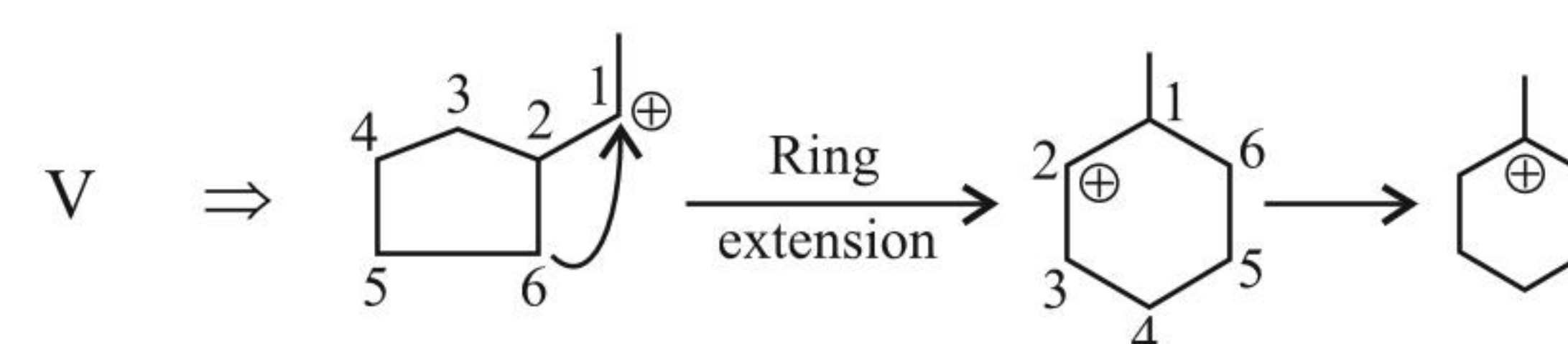
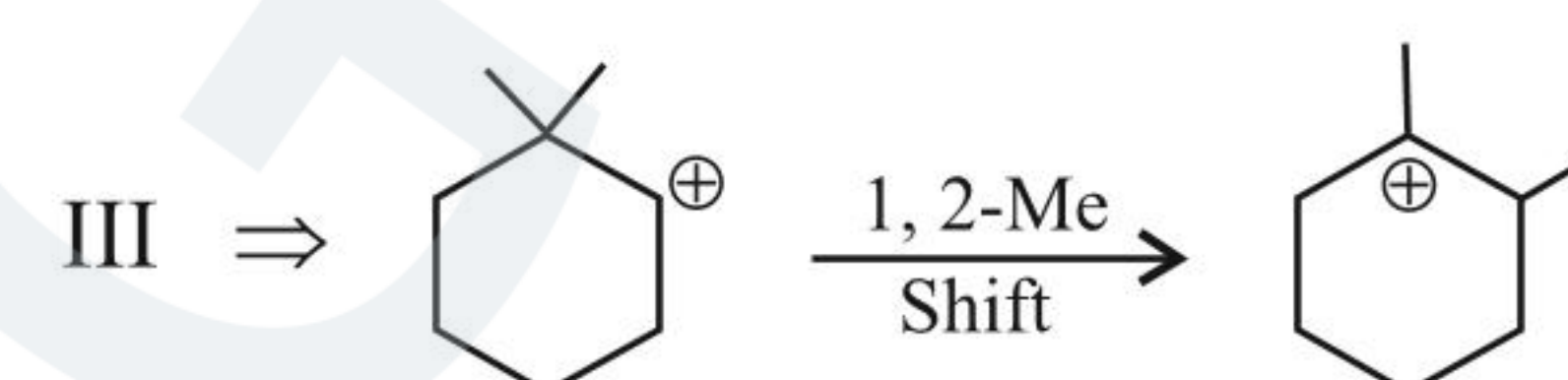
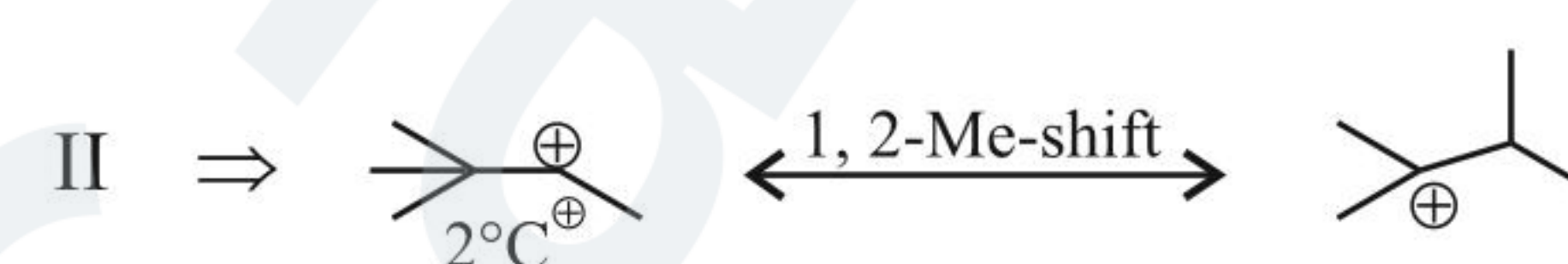
60. (3) Protonation occurs at double bond rather than at (—OH) group.



61. (2) Addition according to anti Markovnikov rule. Overall reaction is hydroboration oxidation.

62. (3)

63. (2) Six alcohols (II, III, V, VII, IX and (X))

64. (4) Alcohols with $\left(\text{CH}_3-\text{CH}-\right)$ group and (a) give iodoform test. For (a) Refer table 2.3 point-(4) part (c)65. (4) EDG (—OCH₃), stabilises carbocation

66. (3) Five reagents (I, II, IV, VI and VII)

VIII (HCl), alone can not convert ROH to RCl, since HCl bond is strong bond, so it requires some catalyst (Lewis acid).

67. (3) Phenolic compounds give colour with neutral FeCl₃

68. (1) Four reagents (I, IV, V and VI)

I (Test for alcohols and converts 1° alcohol to aldehyde, a mild oxidising agent).

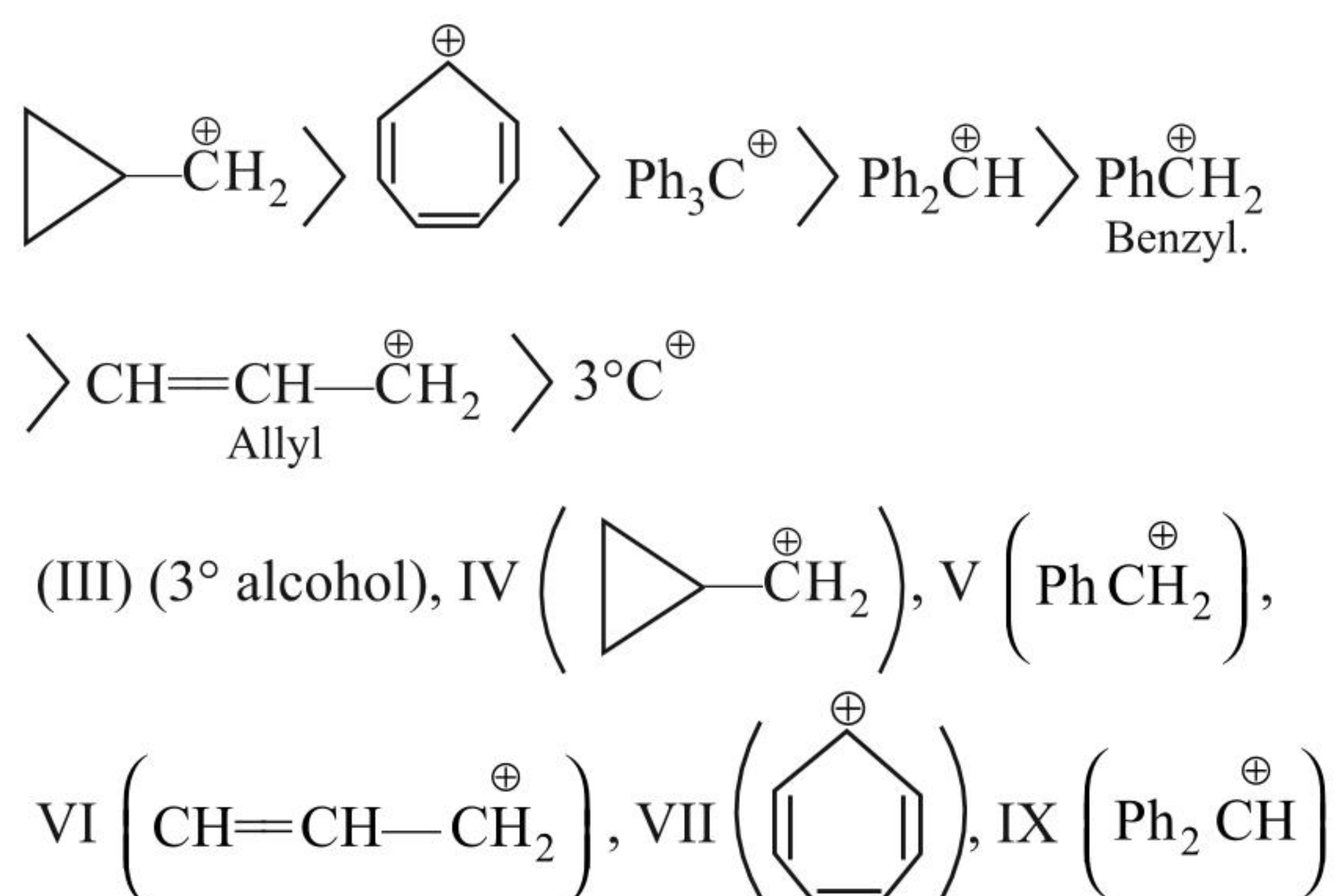
IV, V (variation of PCC), VI (PCC), all are mild oxidising agent and convert 1° alcohol to aldehyde.

II, and III are strong oxidising agent and convert 1° alcohol to acid.

69. (4) Aromatic substitution by nucleophile reaction (ArSN) is favoured by (—NO₂) EWG at o- and p-position.

70. (2) Six compounds (III, IV, V, VI, VII and IX).

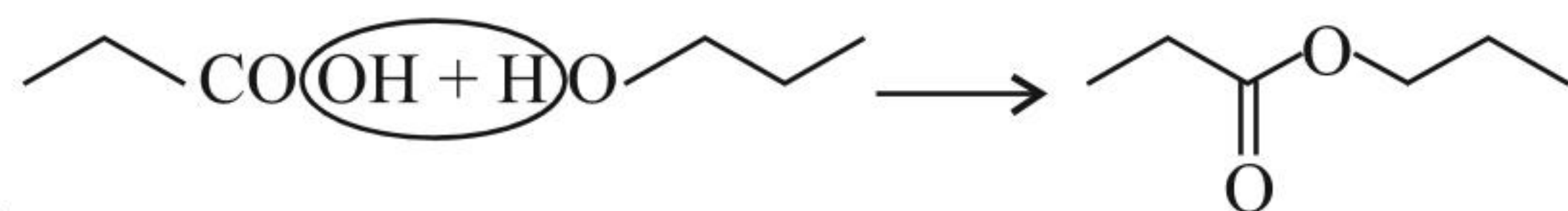
3° alcohols and compounds which form stable carbonium ion gives this test.

Stability of C^+ ion :71. (3) Correct (1) C1CCCCC1=O + HCHO.

(2) Benzene

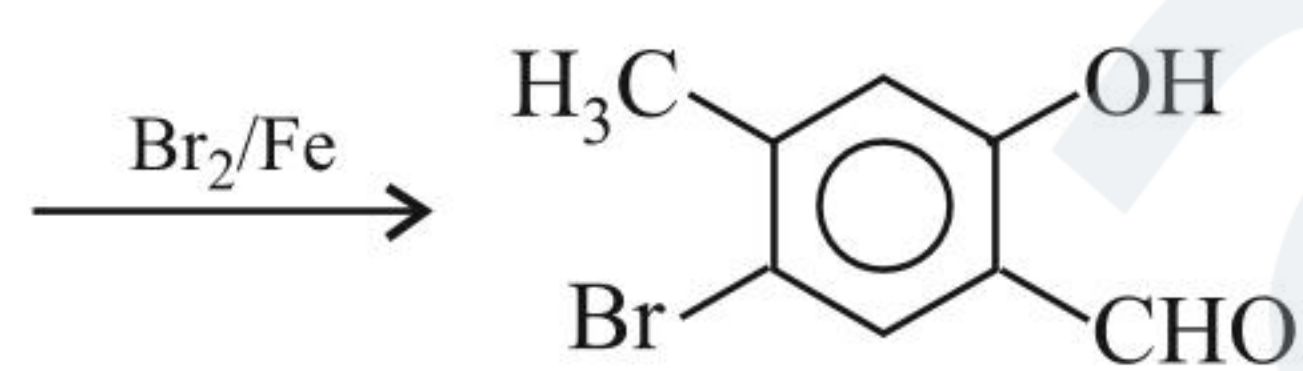
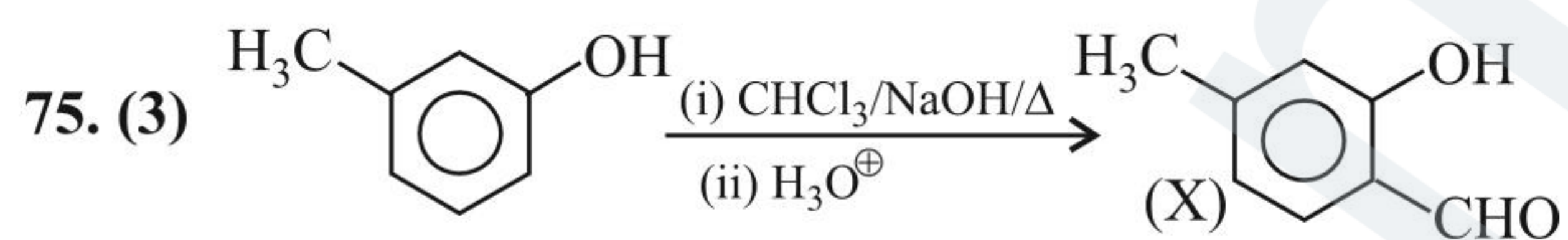
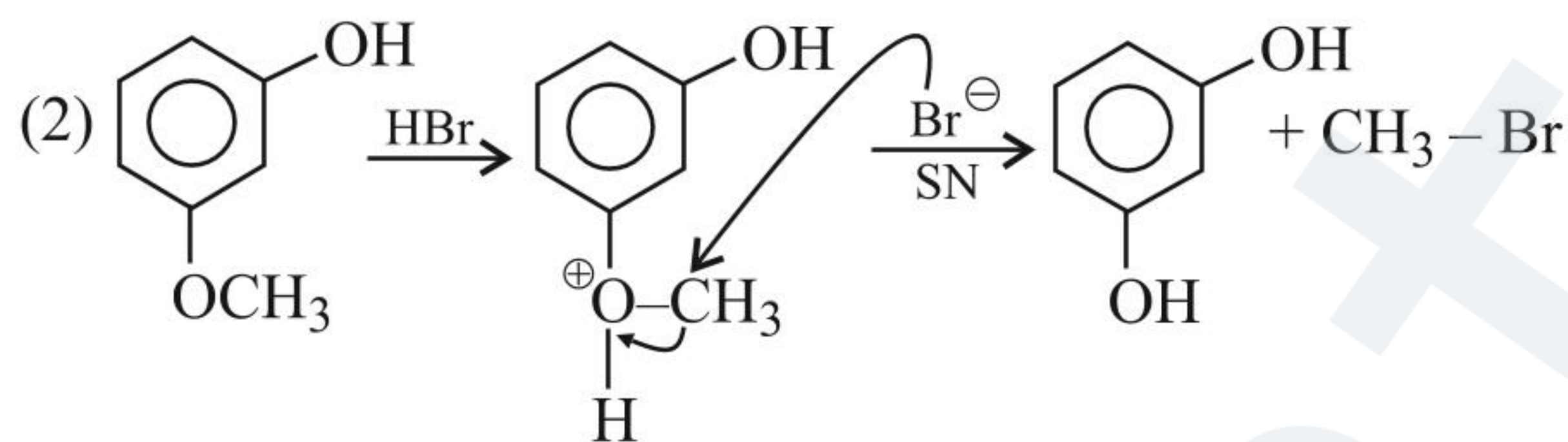
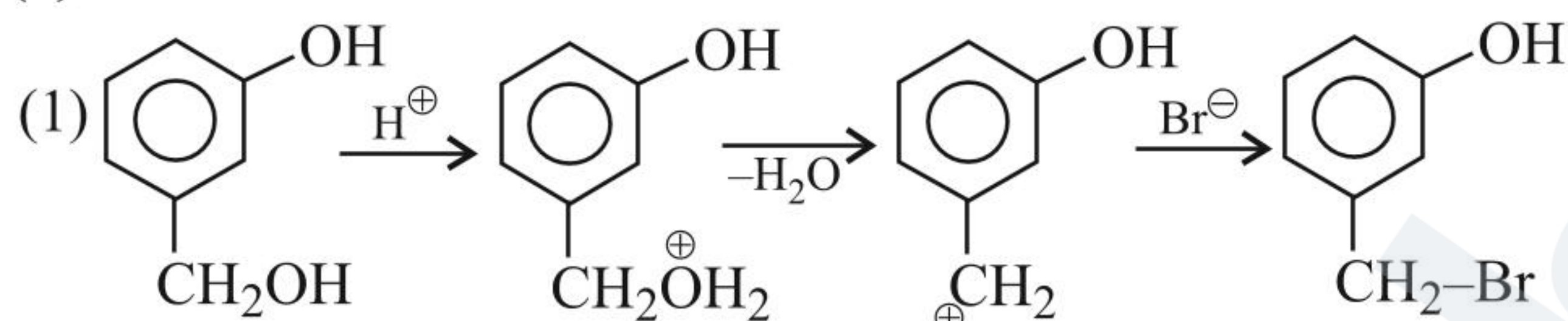
(4) Fries rearrangement (c1ccc(cc1)C(OH)C=C)

72. (2) Correct (2)

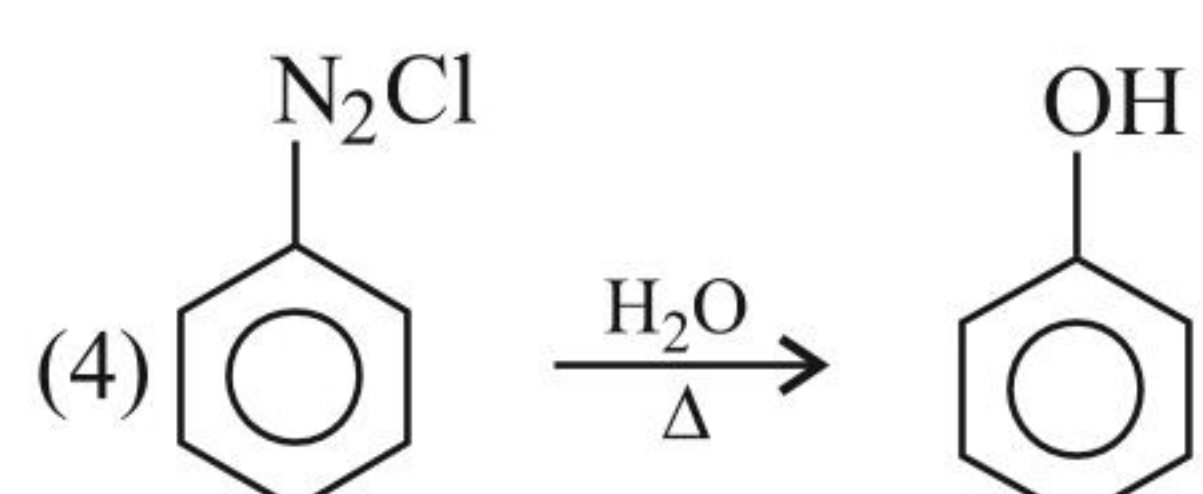
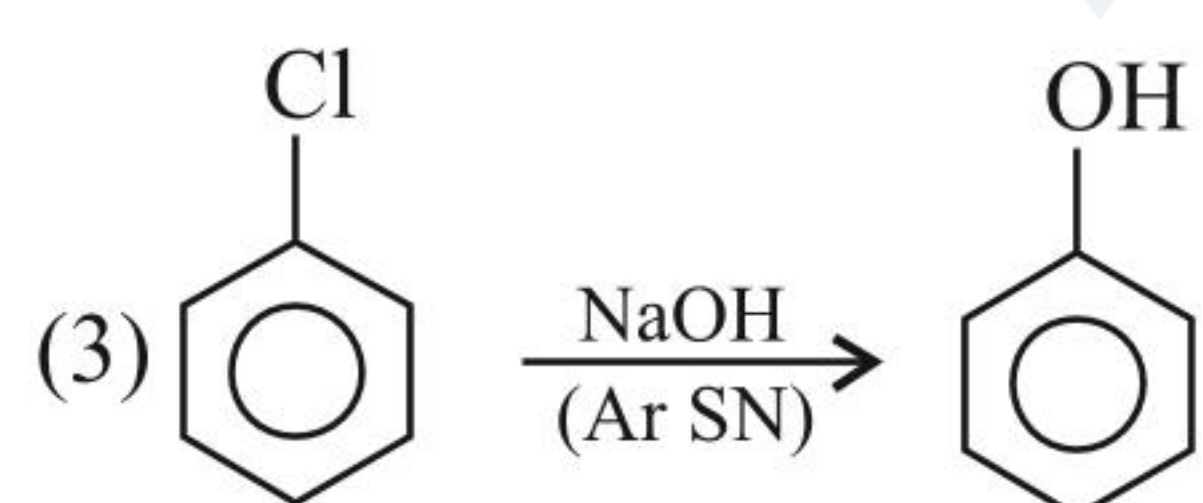
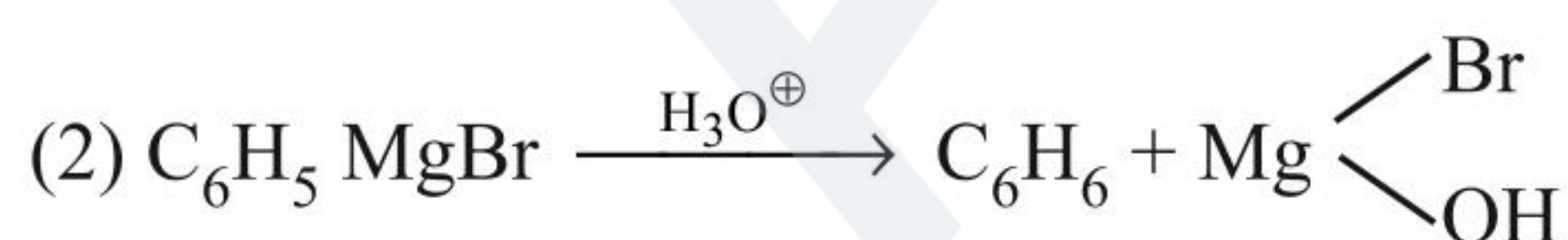
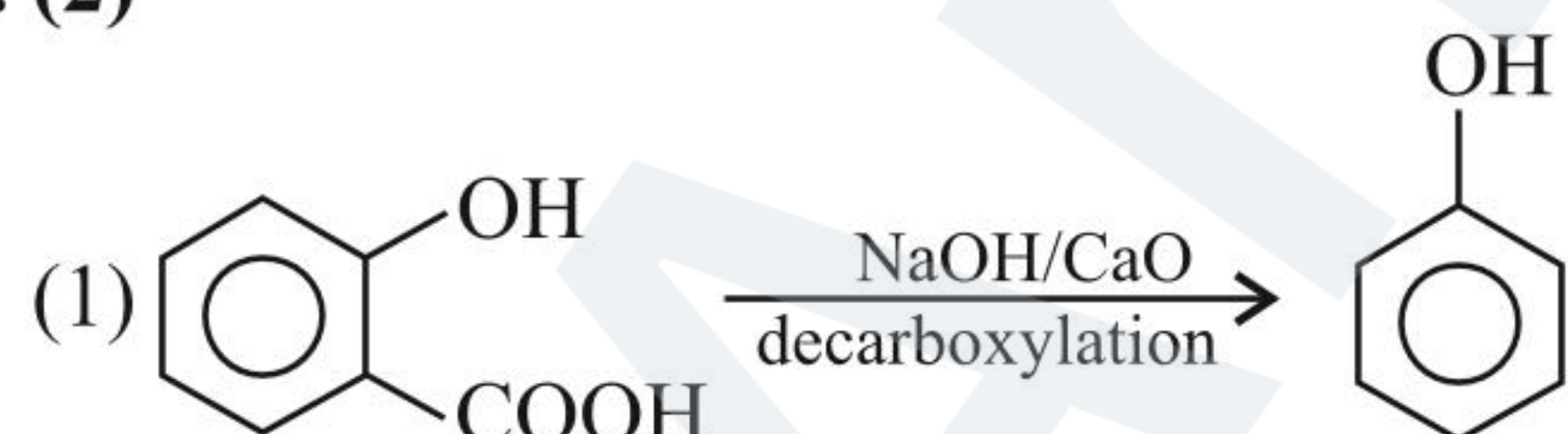


73. (3)

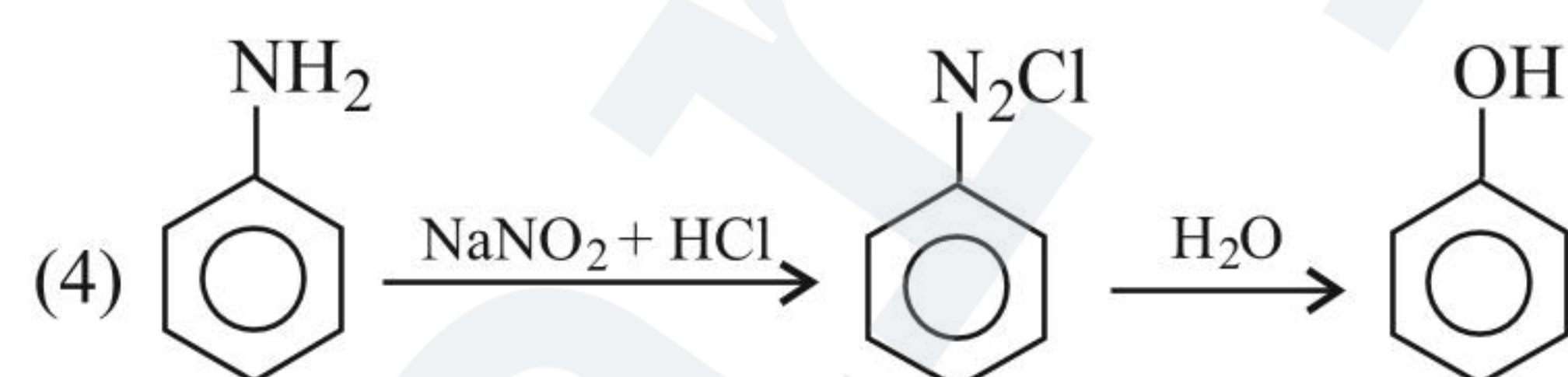
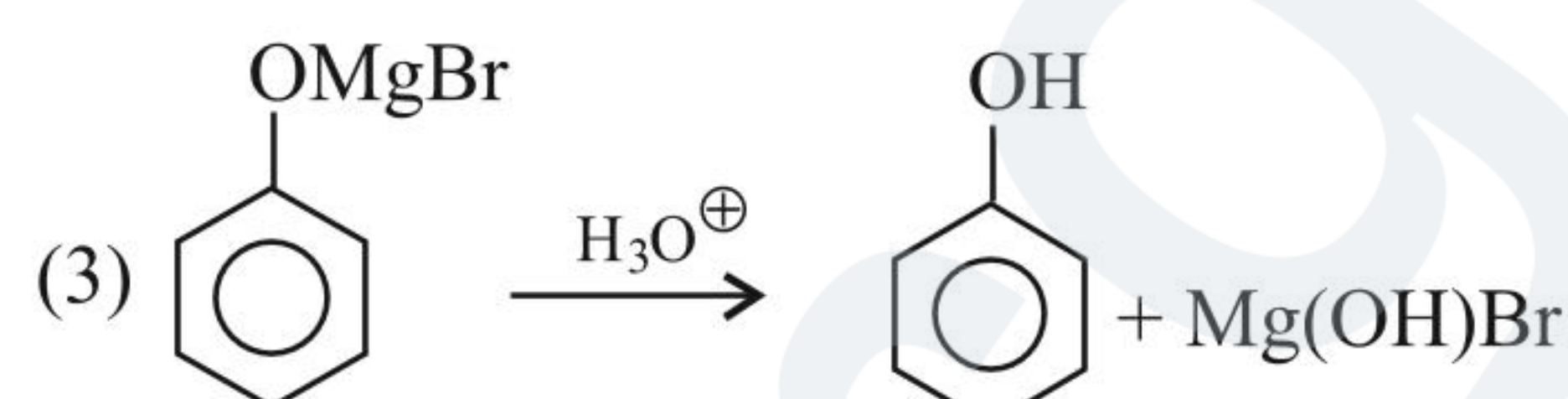
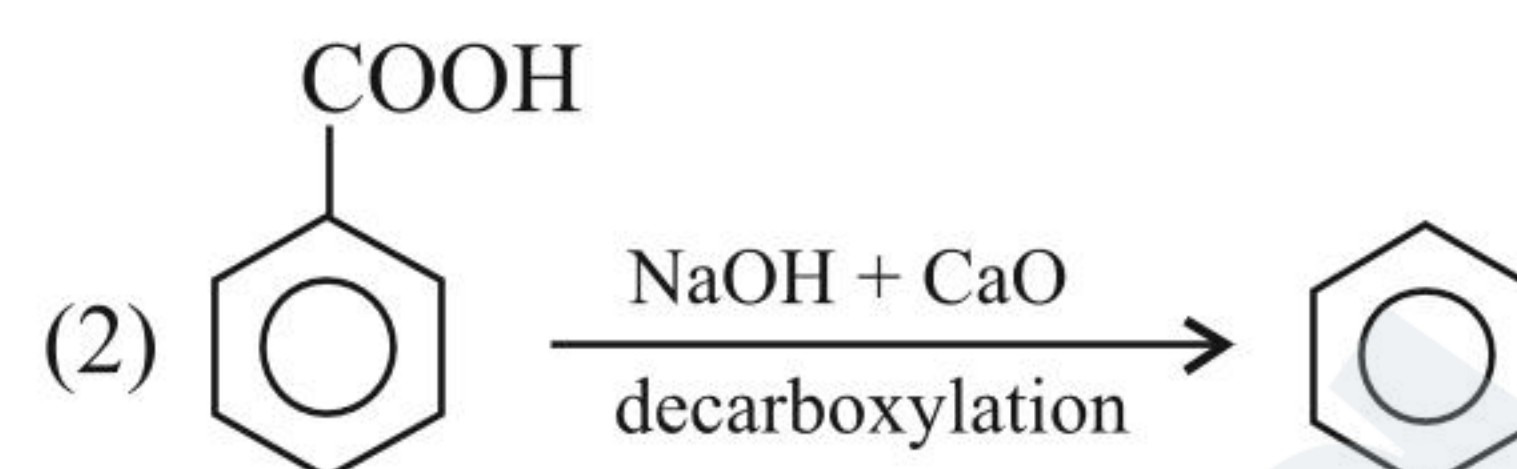
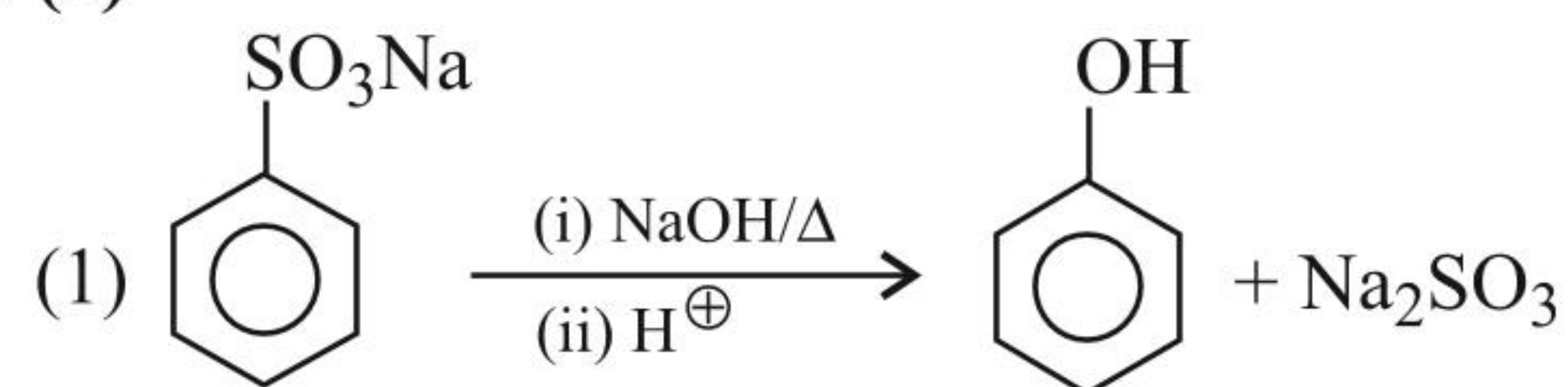
74. (1)

76. (3) *p*-Nitrophenol reacts with NaHCO3.

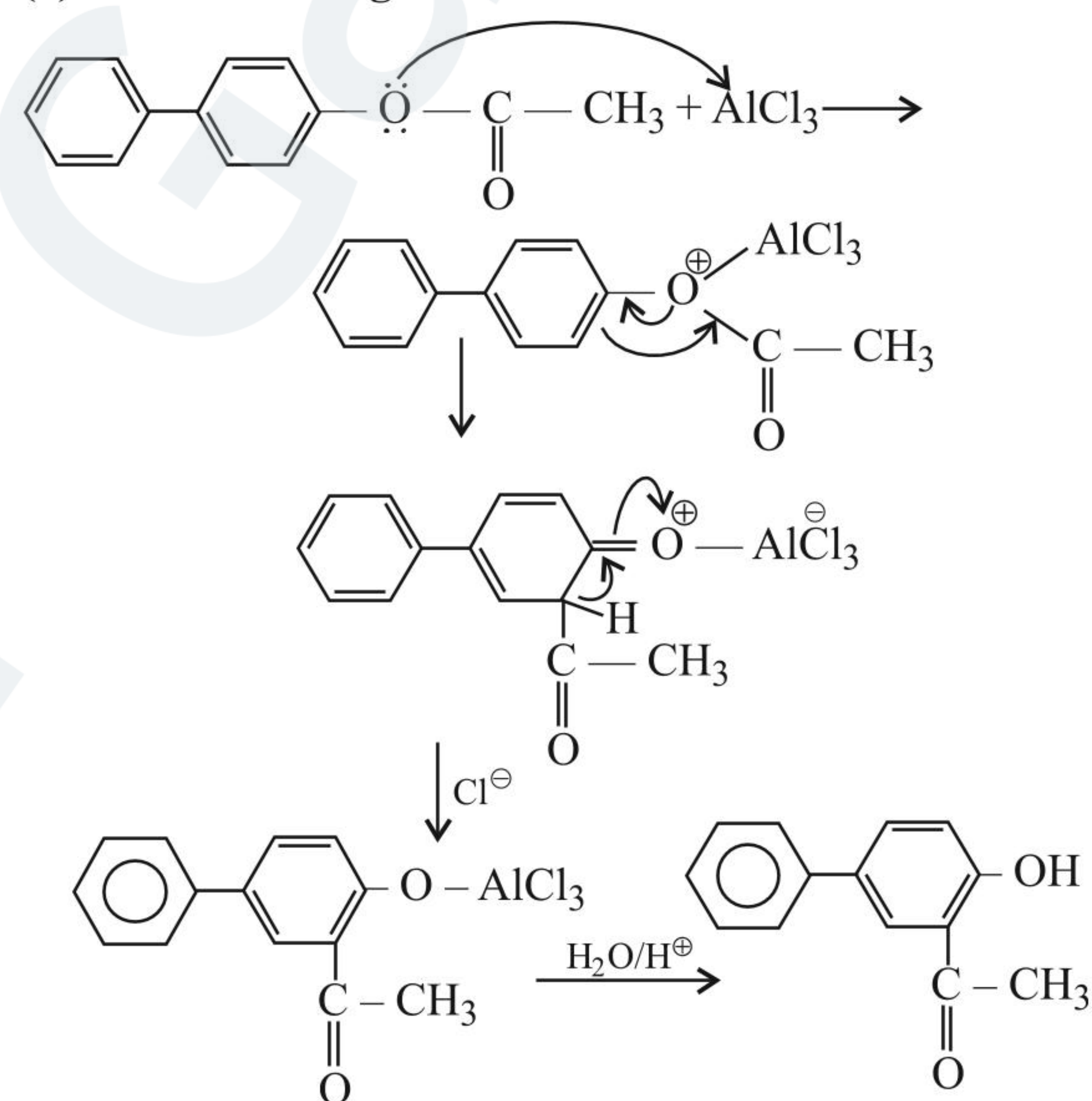
77. (2)



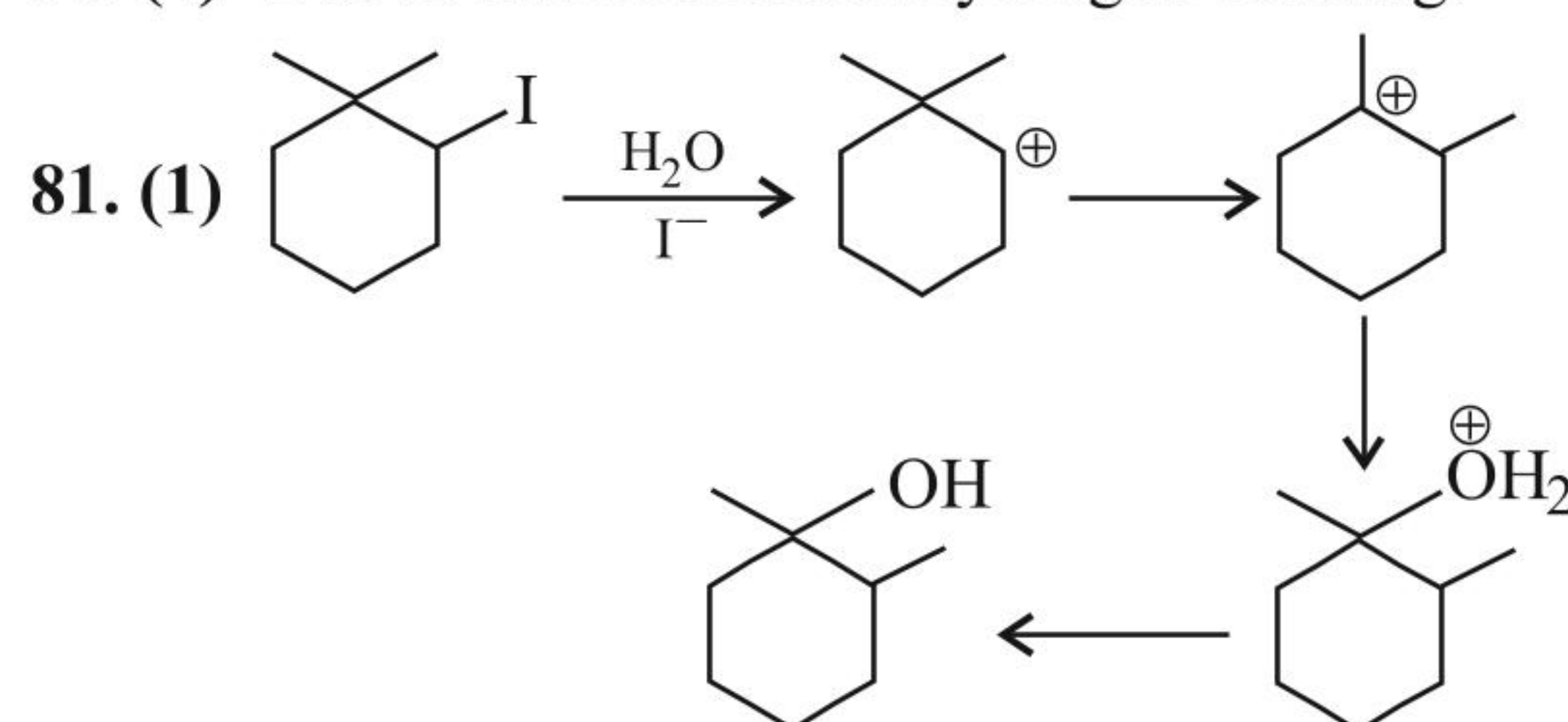
78. (2)



79. (4) Fries rearrangement



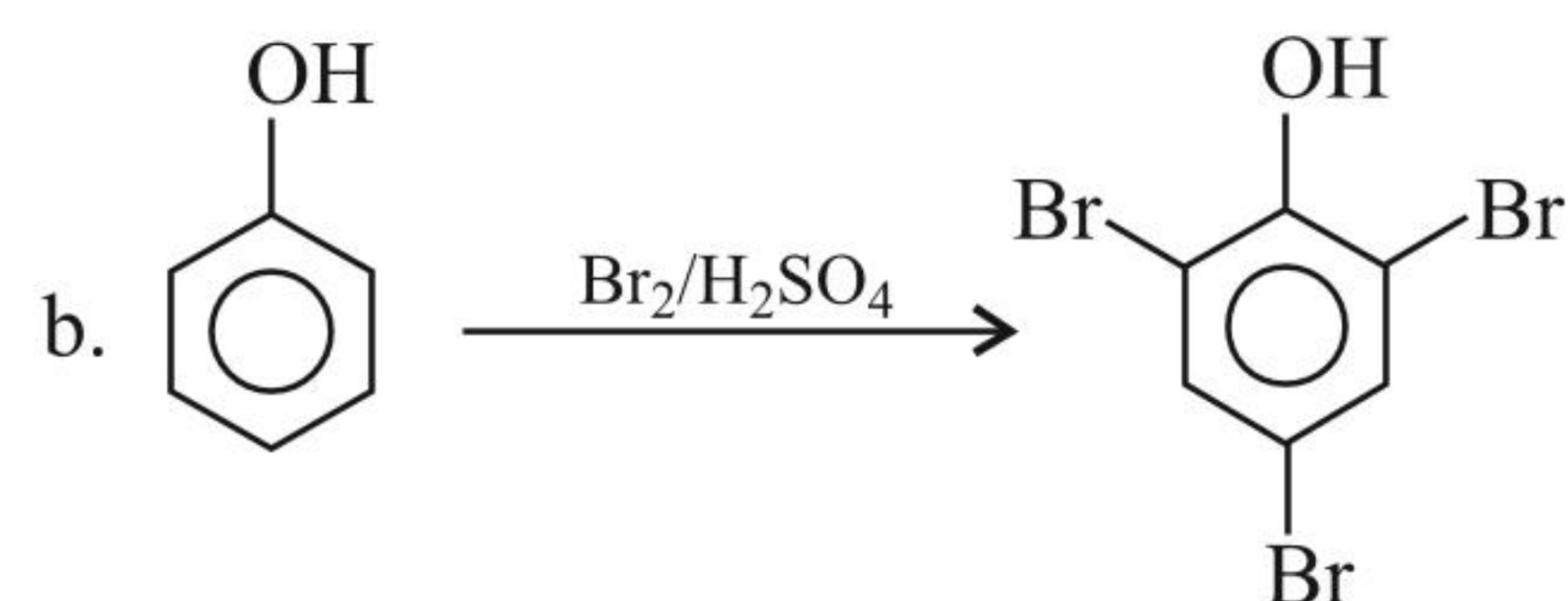
80. (4) Due to intermolecular hydrogen bonding.

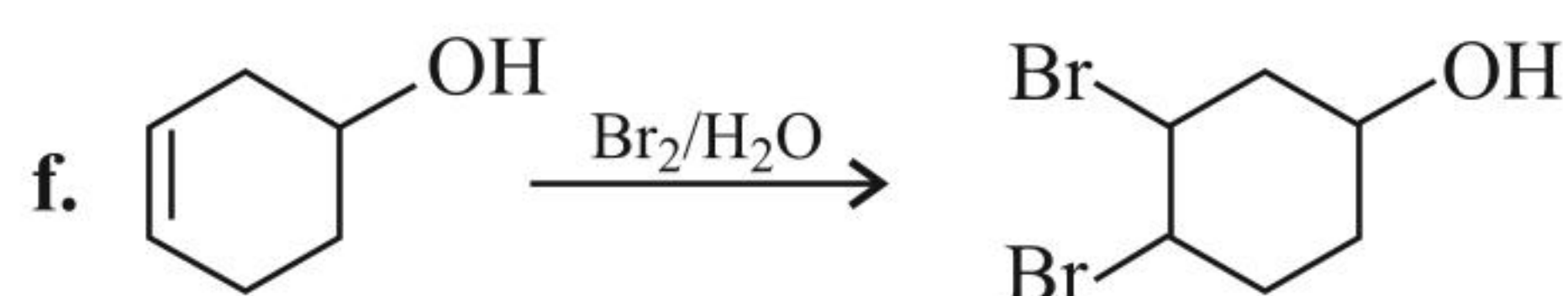
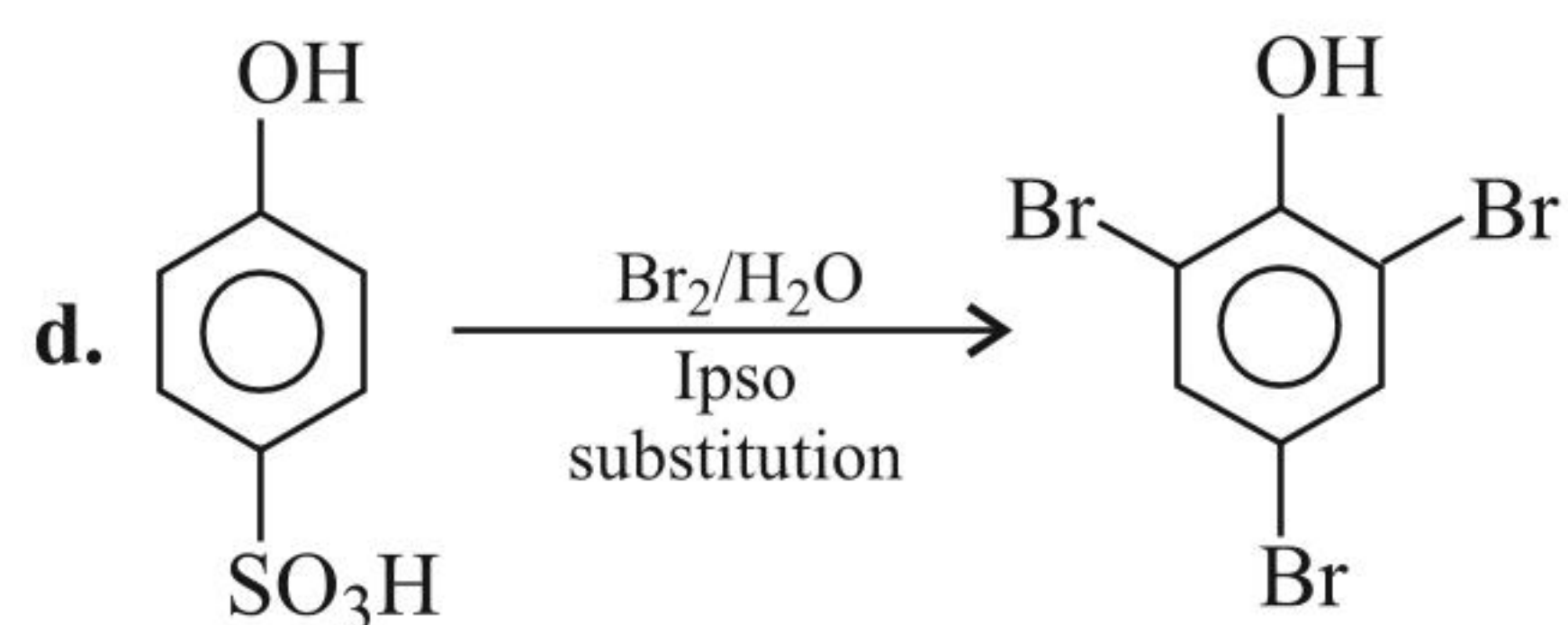
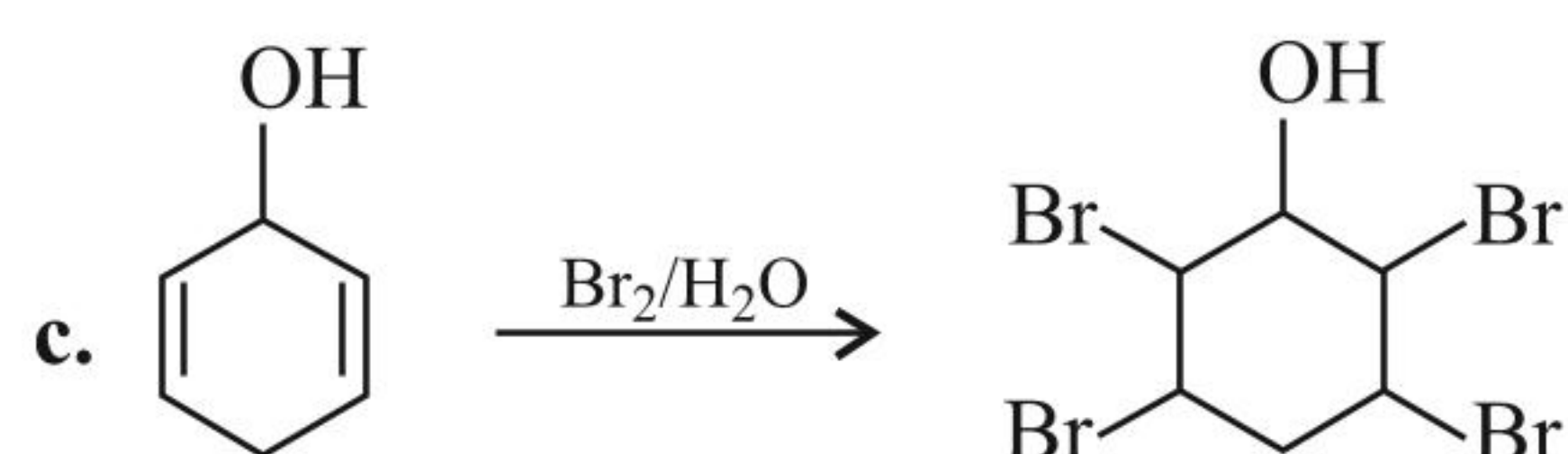


82. (1) Four alcohols which gives +ve test are: (b), (c), (f) and (i).

83. (3) Phenol (b), *o*- or *p*- substituted sulphonic ($-\text{SO}_3\text{H}$) or carboxylic ($-\text{COOH}$) group gives tribromo products with Br2/H2O. (i.e. gives white ppt or decolourises Br2/H2O).Moreover unsaturated compounds containing double or triple bond, decolourises Br2/H2O.Therefore compounds (b), (c) (d) and (f) will decolourises Br2/H2O.

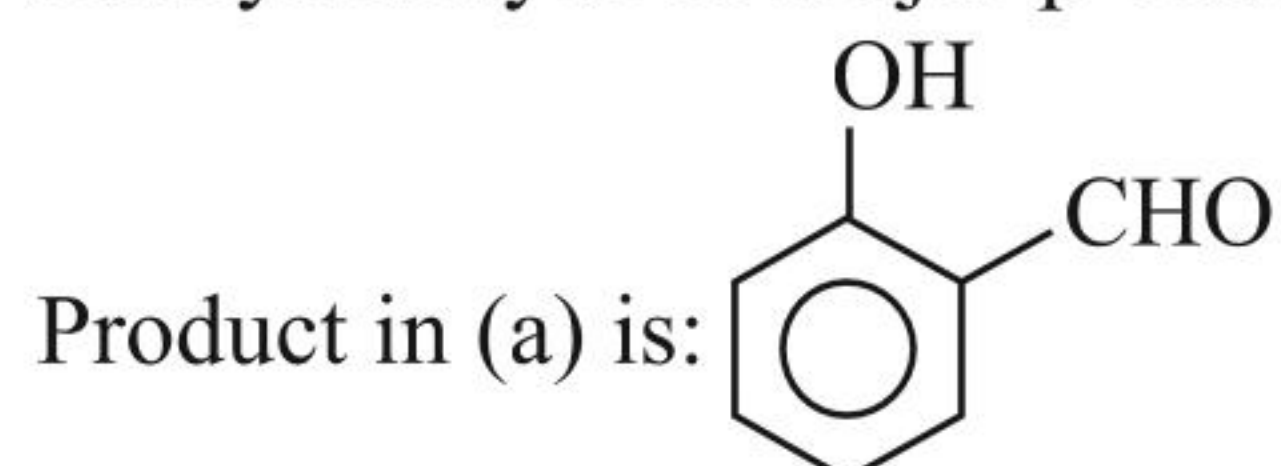
Reactions:



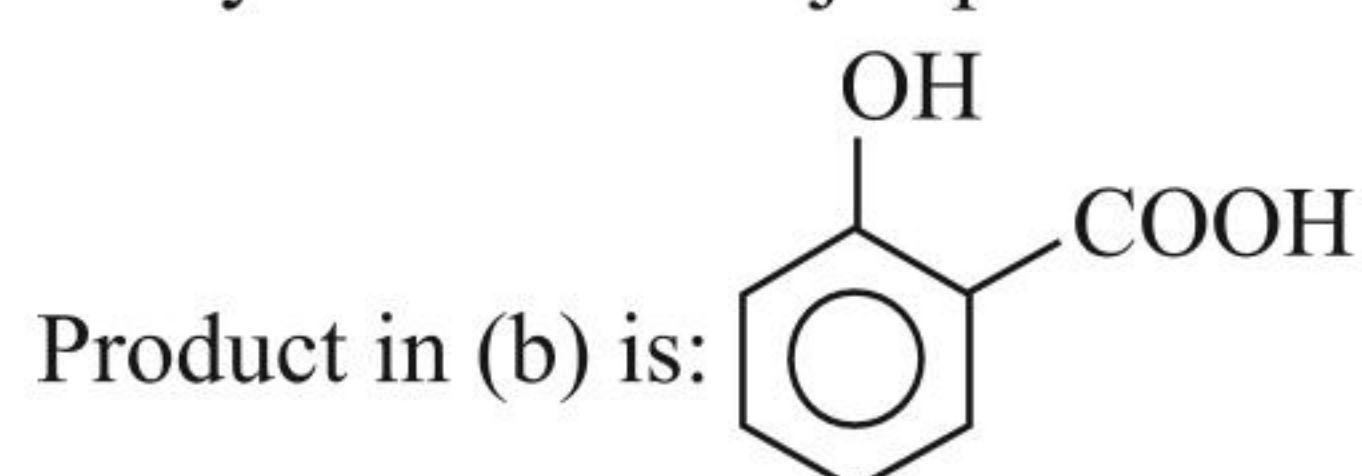


84. (4) Three reaction, (b), (c) and (e) would give salicylic acid as major product.

Reaction (a) is Reimer-Tiemann reaction and would give Salicylaldehyde as major product.



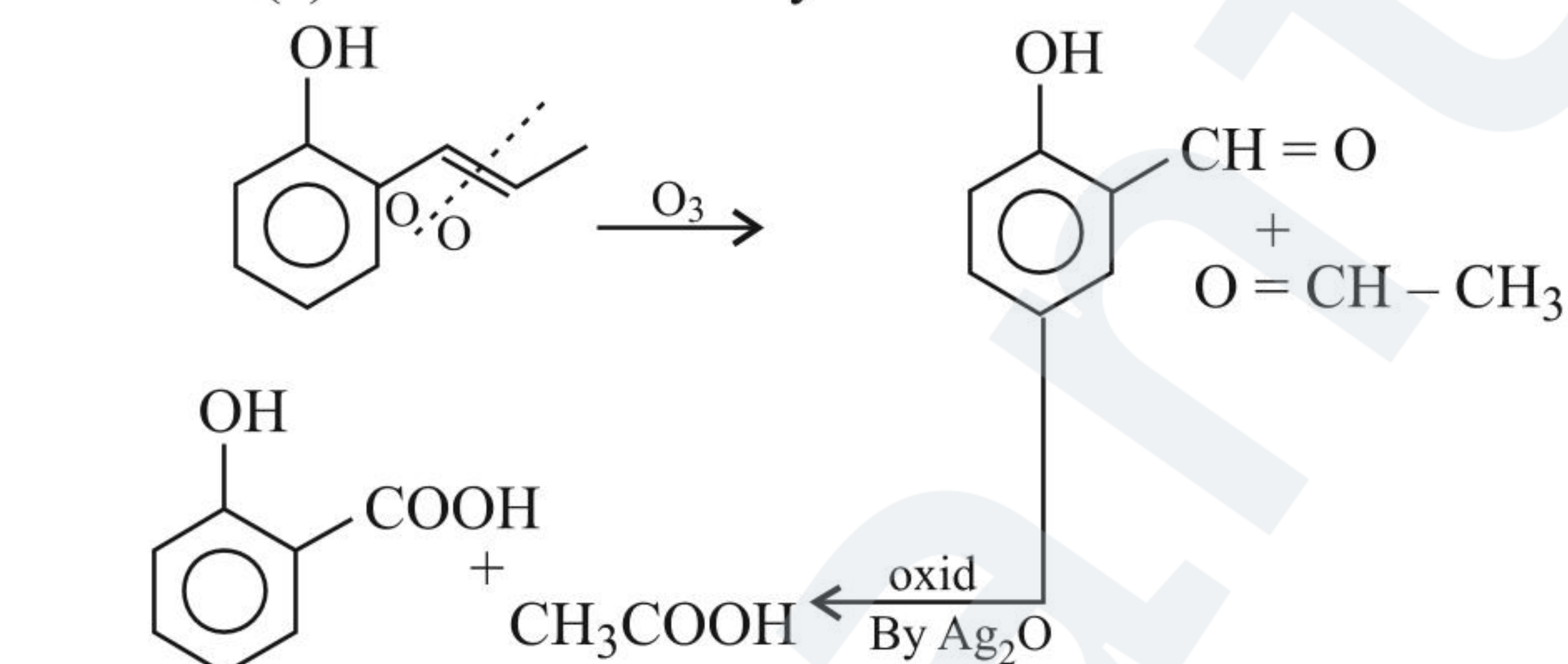
Reaction (b) is Kolbe Schmitt reaction, and would give salicylic acid as major product.



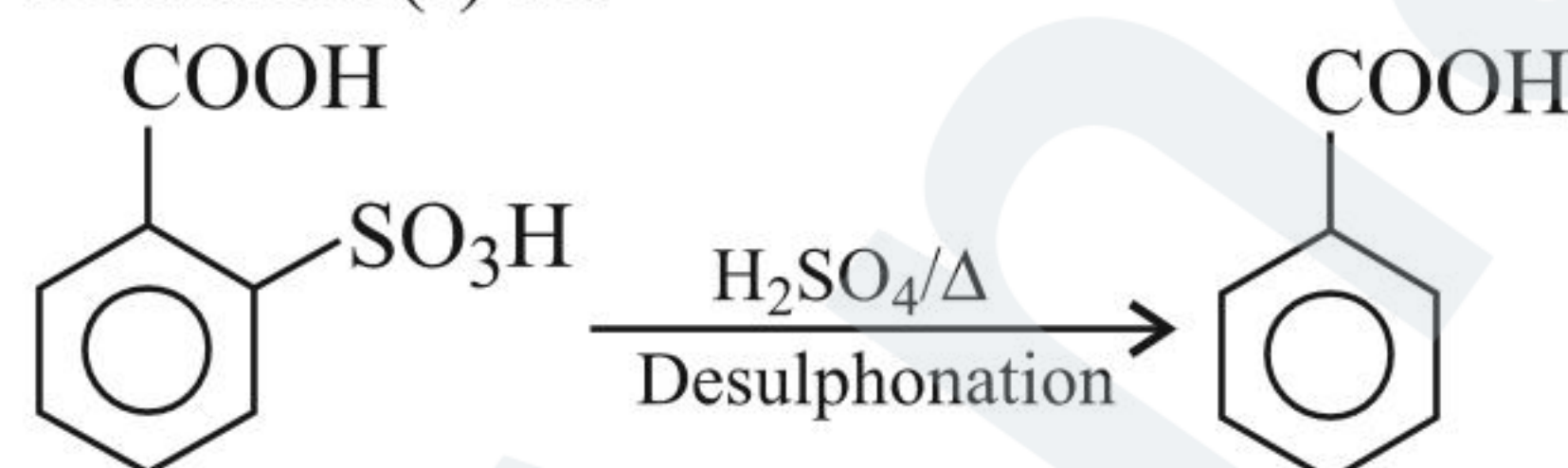
Reaction (c) is extension of Reimer-Tiemann reaction and give salicylic acid as major product.

Reaction (d) is Reimer-Tiemann reaction and give salicylaldehyde as major product.

Reaction (e) is oxidative ozonolysis:



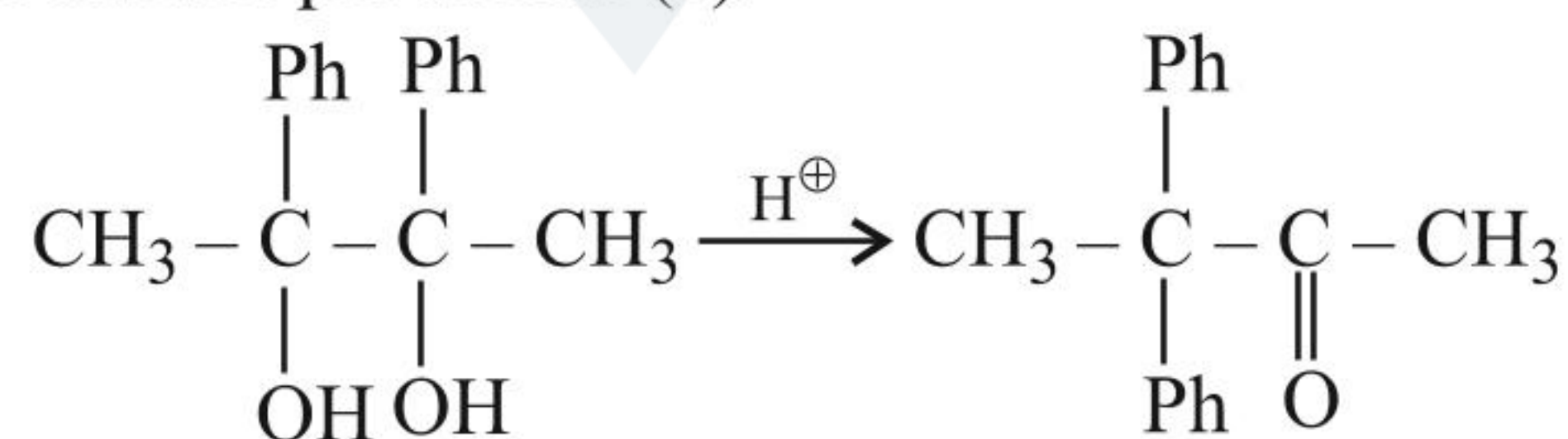
Reaction (f) is:



Hence the answer is:

Three reactions (b, c and e) would give salicylic acid as major product.

85. (3) The correct product is (c).



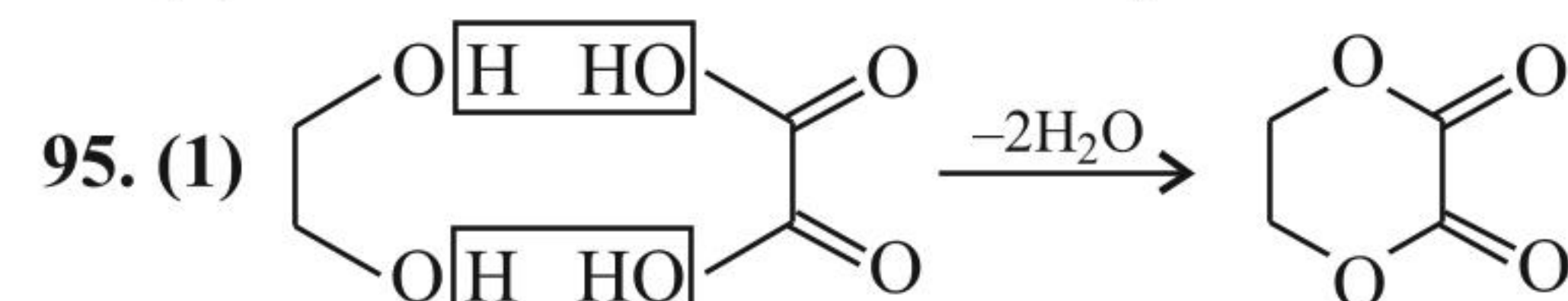
86. (2) Five reagents are: a, b, c, e, and g.

87. (3) 88. (2) 89. (2) 90. (3) 91. (2)

92. (4)

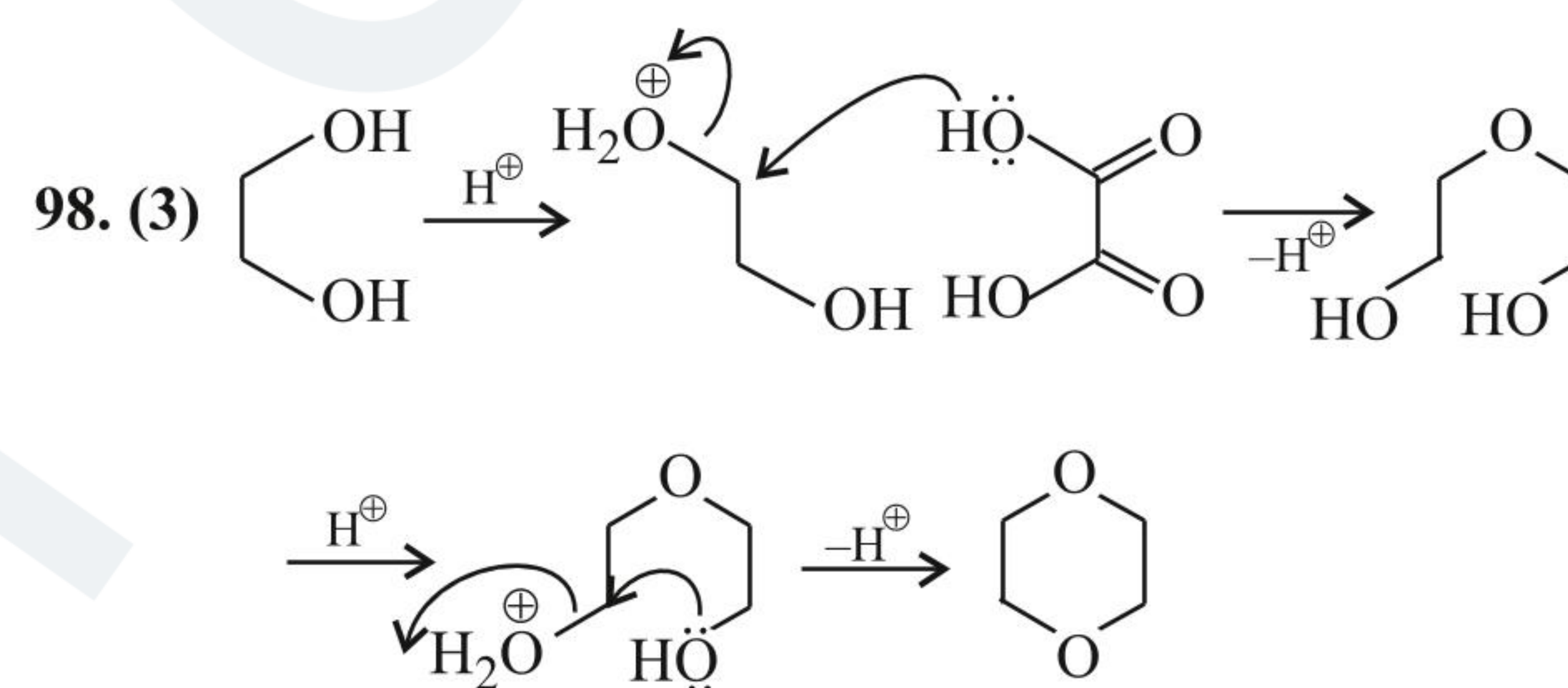
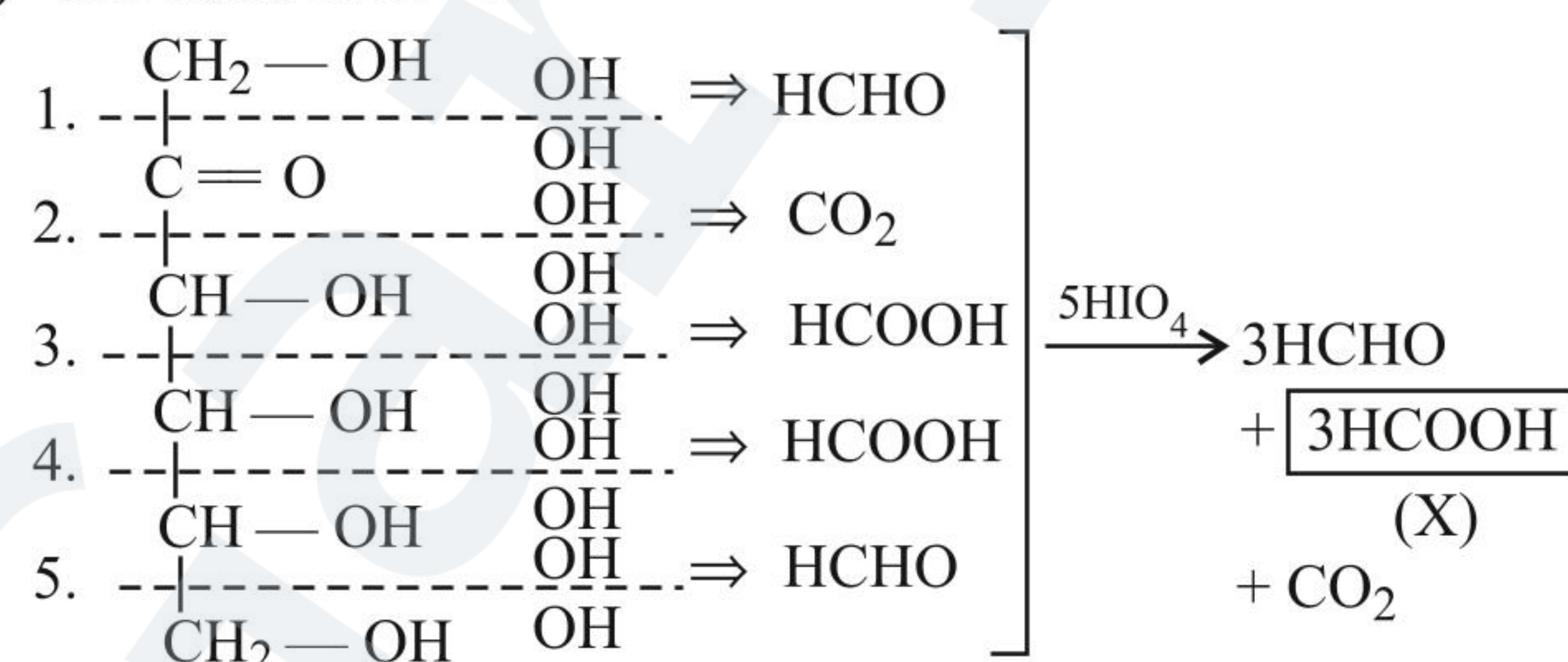
93. (2) In esterification, alcohol contributes H and acid gives OH in loss in water.

94. (1) Greater the steric hindrance, slower is the oxidation.

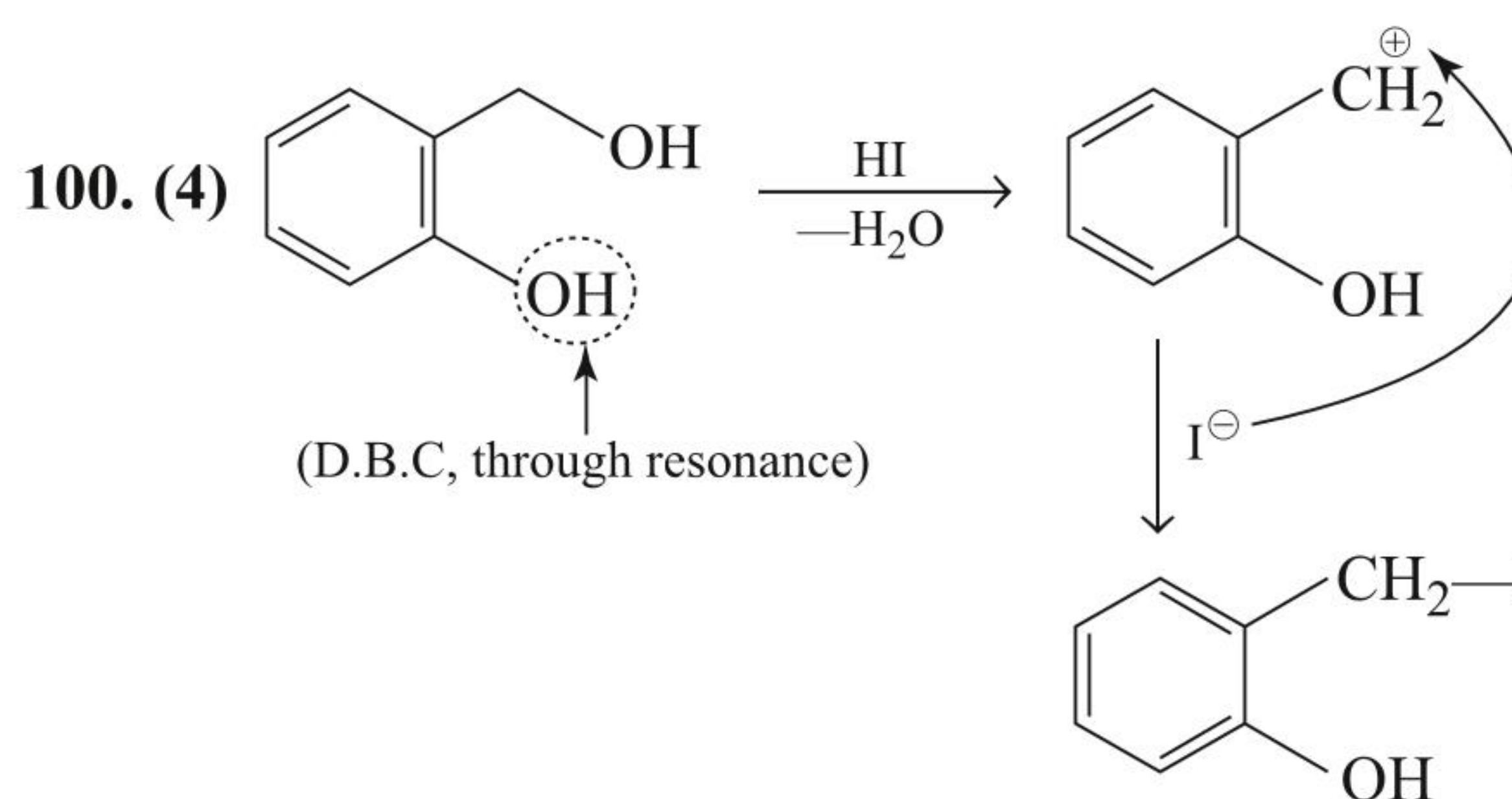
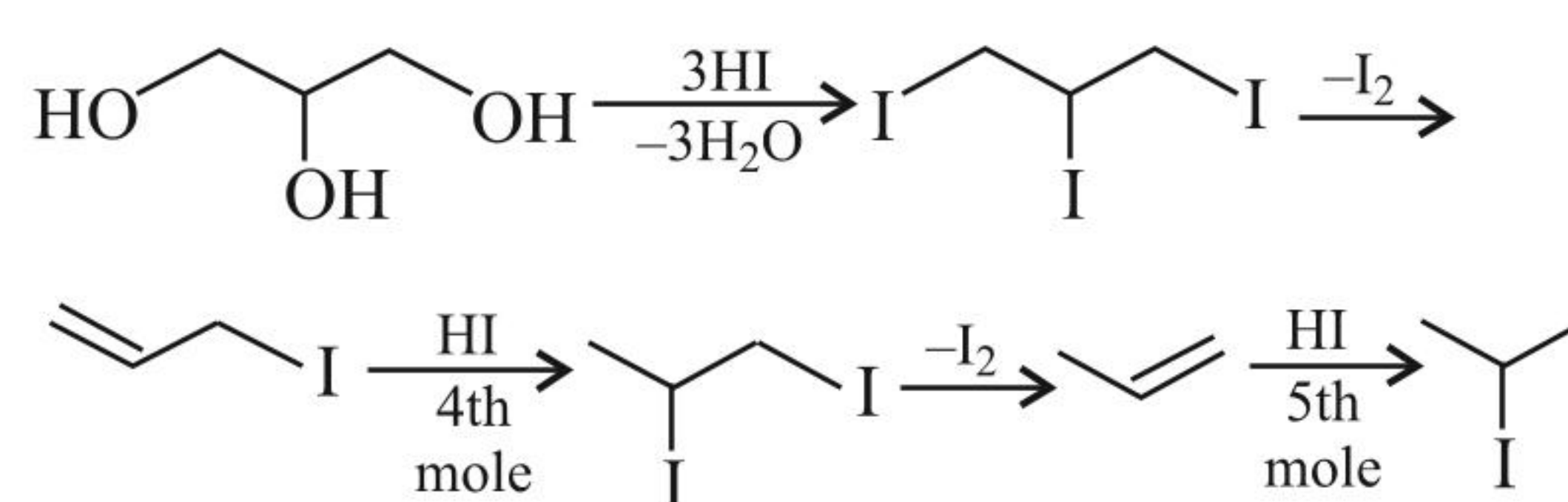


96. (1) All these compounds have $\left[\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \end{array} \right]$ glycolic groups, hence, they are oxidised by periodic acid (HIO_4).

97. (3) The value of X = 3



99. (2) 5 moles:



101. (3) $\text{RX} \Rightarrow$ Alkyl chloride

$\text{RO}^- \Rightarrow$ Vinyl alkoxide

102. (2) Only the acidic ArOH is converted first to its conjugate base than to Me ether.

103. (1) The cleavage of $(\text{C}-\text{OH})$ bond is feasible rather than cleavage of $(\text{Ar}-\text{OH})$ bond because of resonance stabilisation in ArOH .

104. (2) 105. (3) 106. (2) 107. (3) 108. (1)

109. (3) 110. (2) 111. (1) 112. (4)

113. (4) Six types of ethers cannot be prepared by Williamson's synthesis.

	RX	RONa
1.	2° C	2°
2.	2° C	3°
	3° C	2°
3.	3° C	3°
4.	Ar	Ar
5.	Vinyl	Vinyl
6.	Neopentyl	Neopentyl

- (1) Not feasible, RX = 3°, RONA = 3°
 (2) Not feasible, RX = 2°, RONA = 2°
 (3) Not feasible, ArX, ArONa
 (4) Feasible, RX = 1°, ArONa

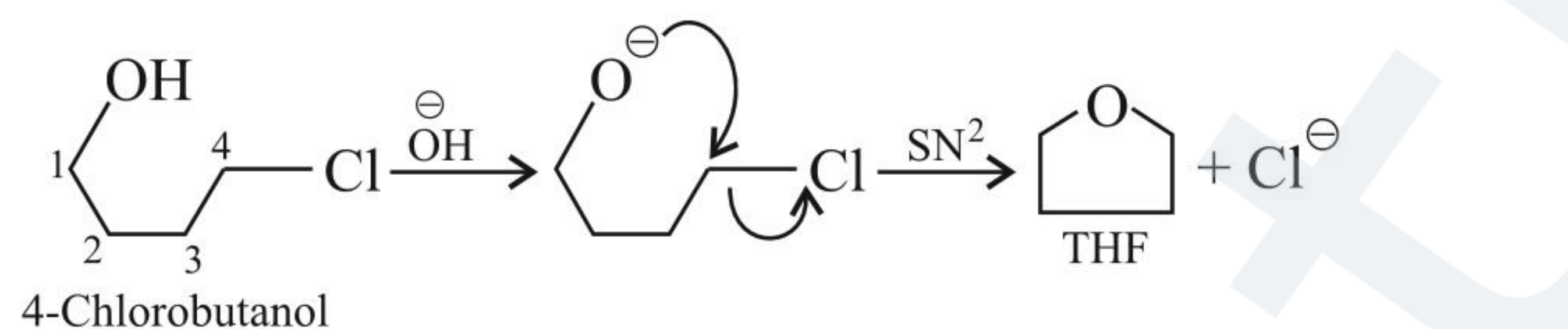
114. (3)

- (1) Not feasible, RX = Neopentyl, RONA = Neopentyl
 (2) Not feasible, RX = Vinyl halide, RONA = Vinyl
 (3) Feasible, RX = 1°, RONA = 3°
 (4) Not feasible, ArX, RONA = 1°

115. (1) ii > iv > iii > i (allyl chloride > 1° RBr > 1° RCl > neopentyl bromide. (R—Br) bond is weaker than (R—Cl) bond. S_N2 reaction is faster with (R—Br) than with (R—Cl).

116. (3)

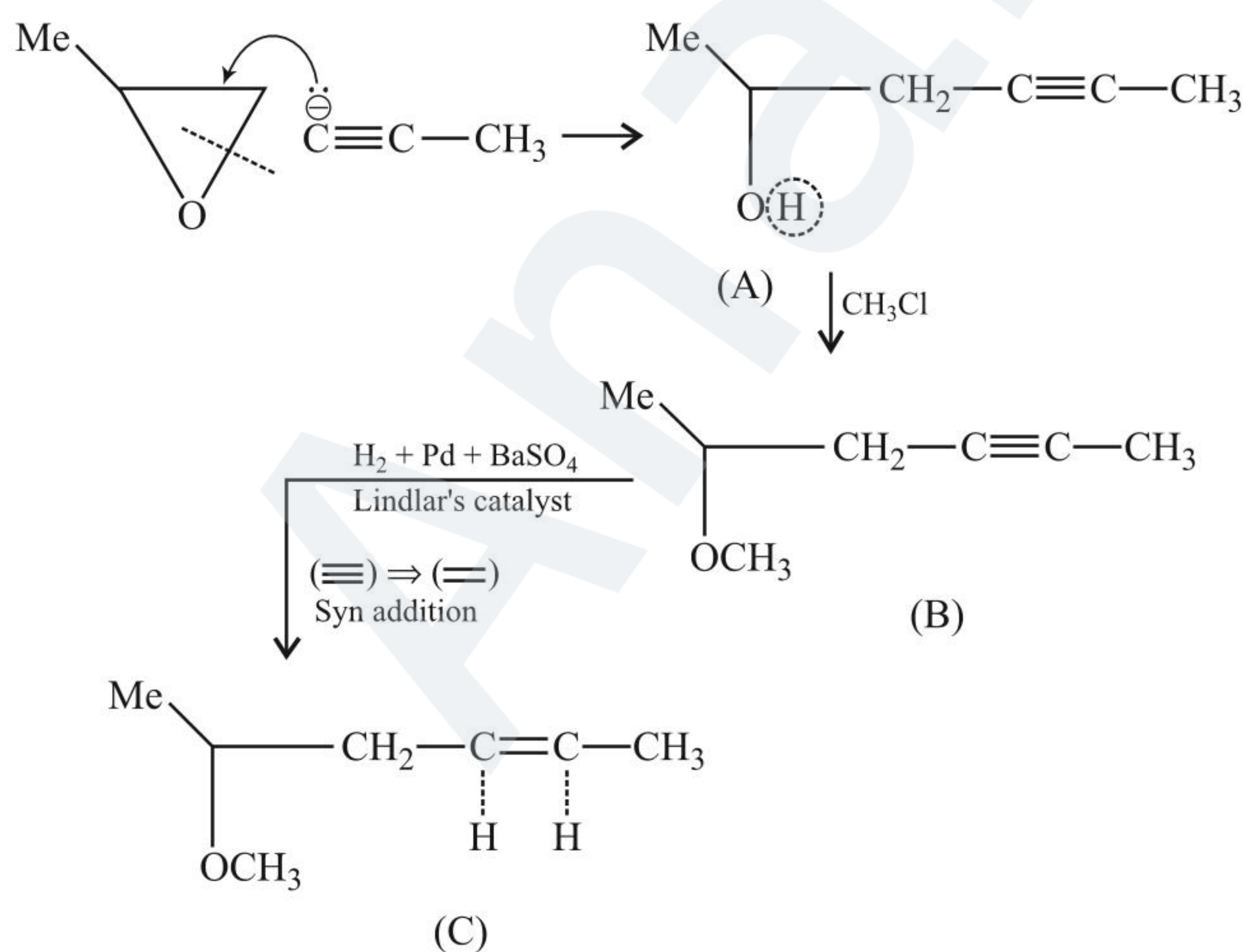
117. (2) This is an example of intramolecular S_N2 Williamson's reaction.



118. (2)

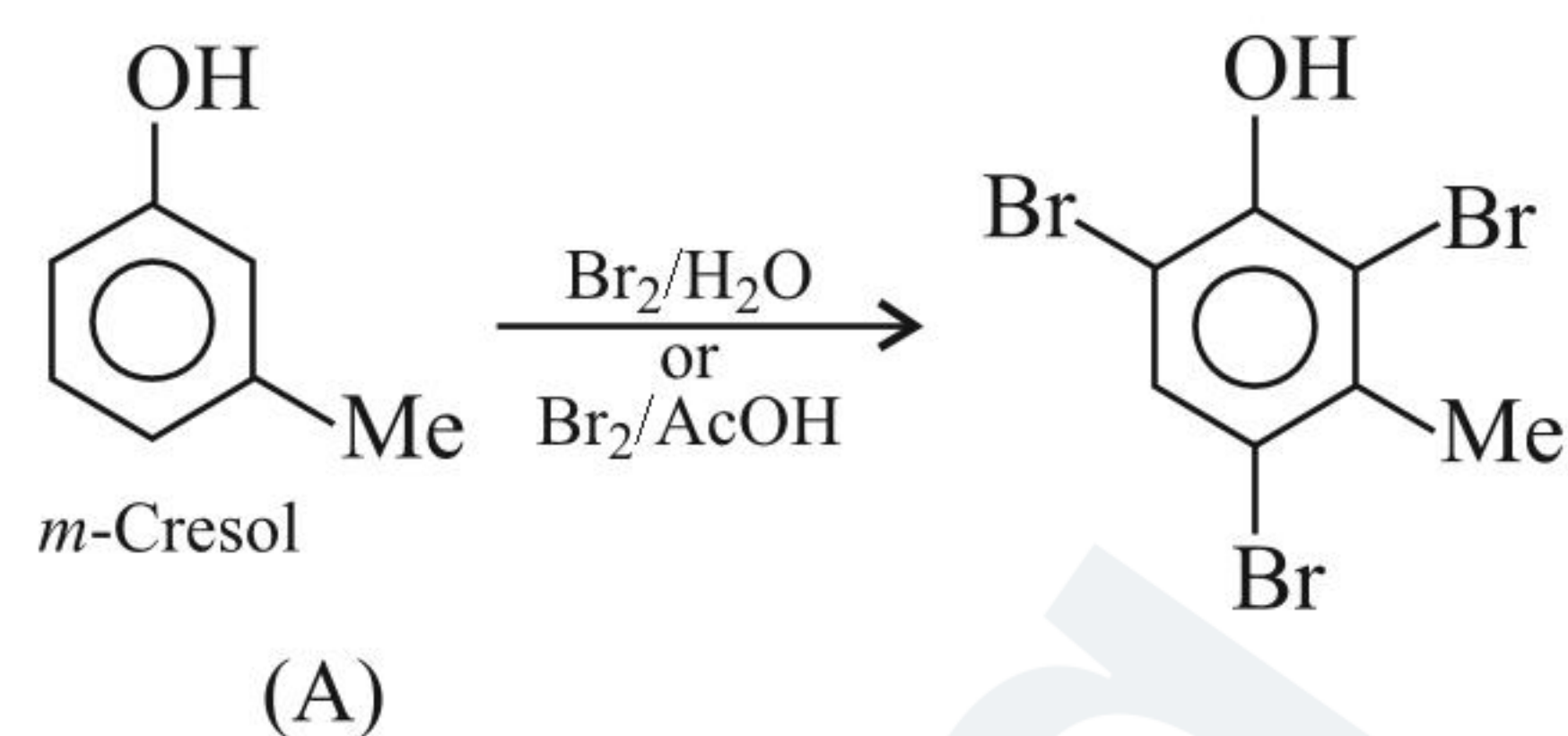
119. (4) Intermolecular dehydration of two different 1° alcohols gives a mixture of ethers, ROR, ROR', and R'OR'.

120. (1)

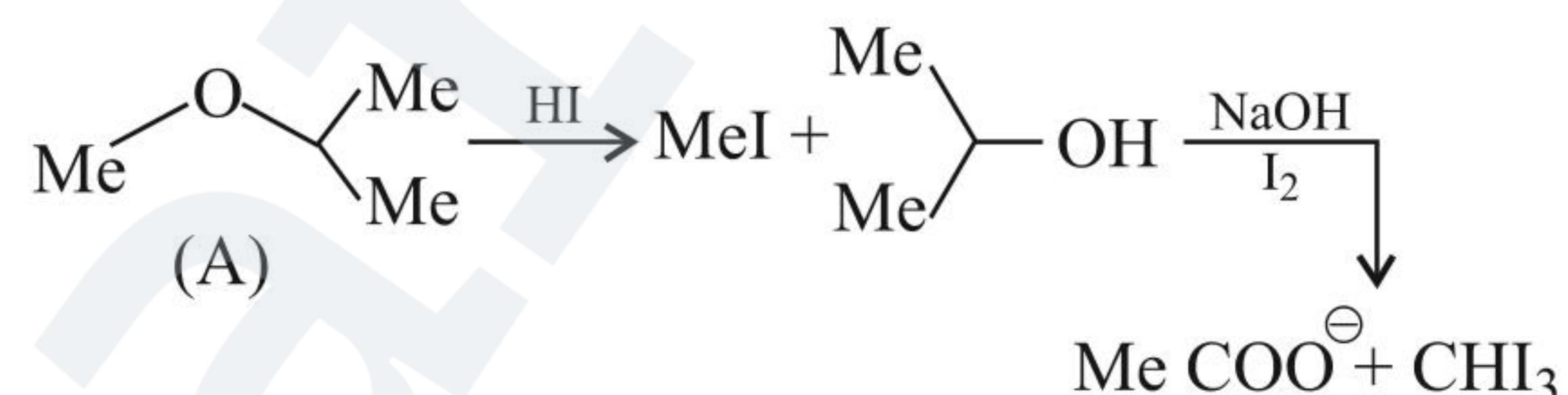


121. (3) Four DU in A and (C:H ≈ 1:1) suggest benzene ring with one extra C atom. Reactivity with NaOH and FeCl₃ suggests (A) to be a phenol. The formation of a tribromo product suggests that *o*-

and *p*-positions are vacant. So methyl group should be present at *m*-position. Hence, (A) is *m*-cresol.

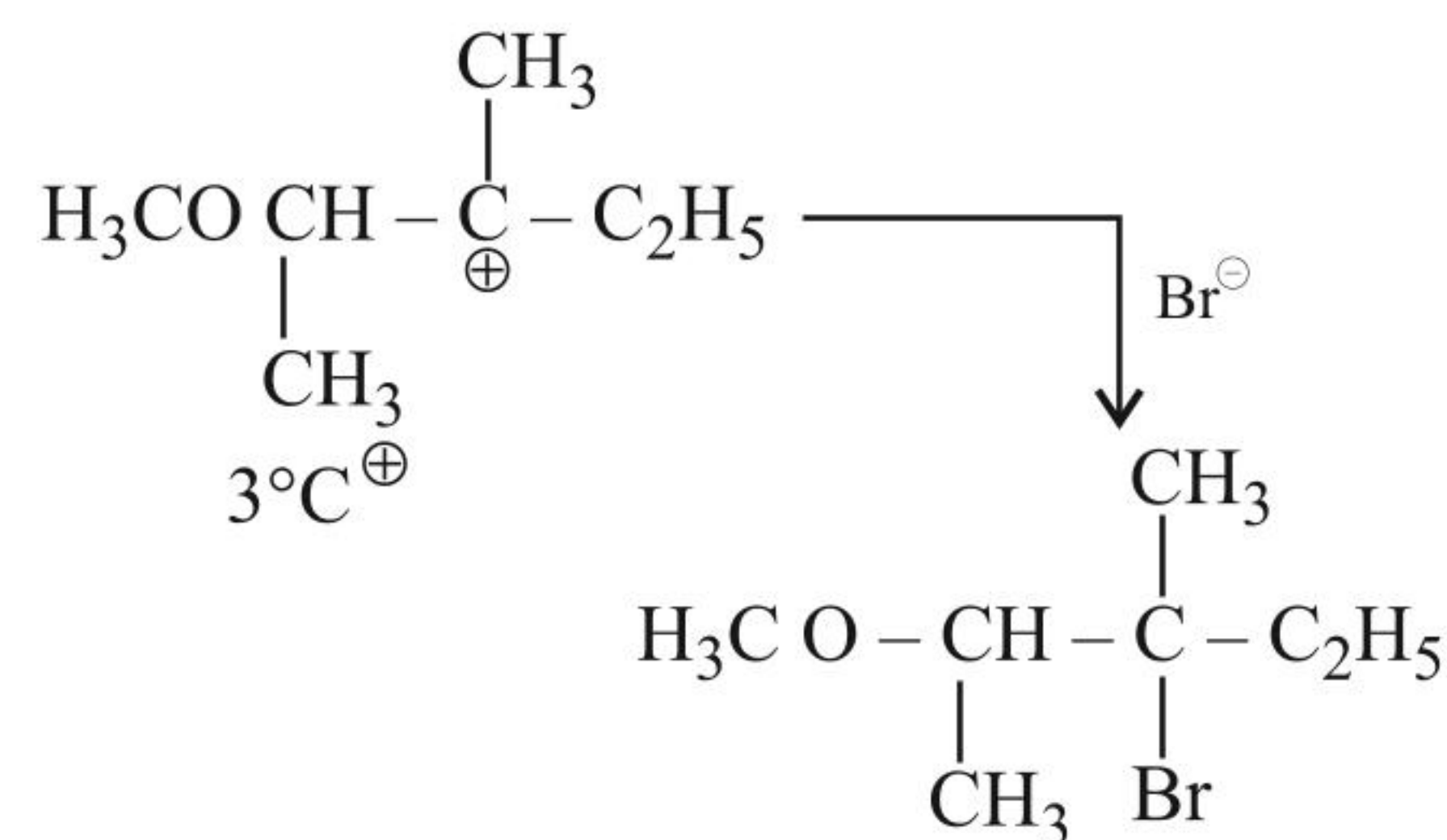
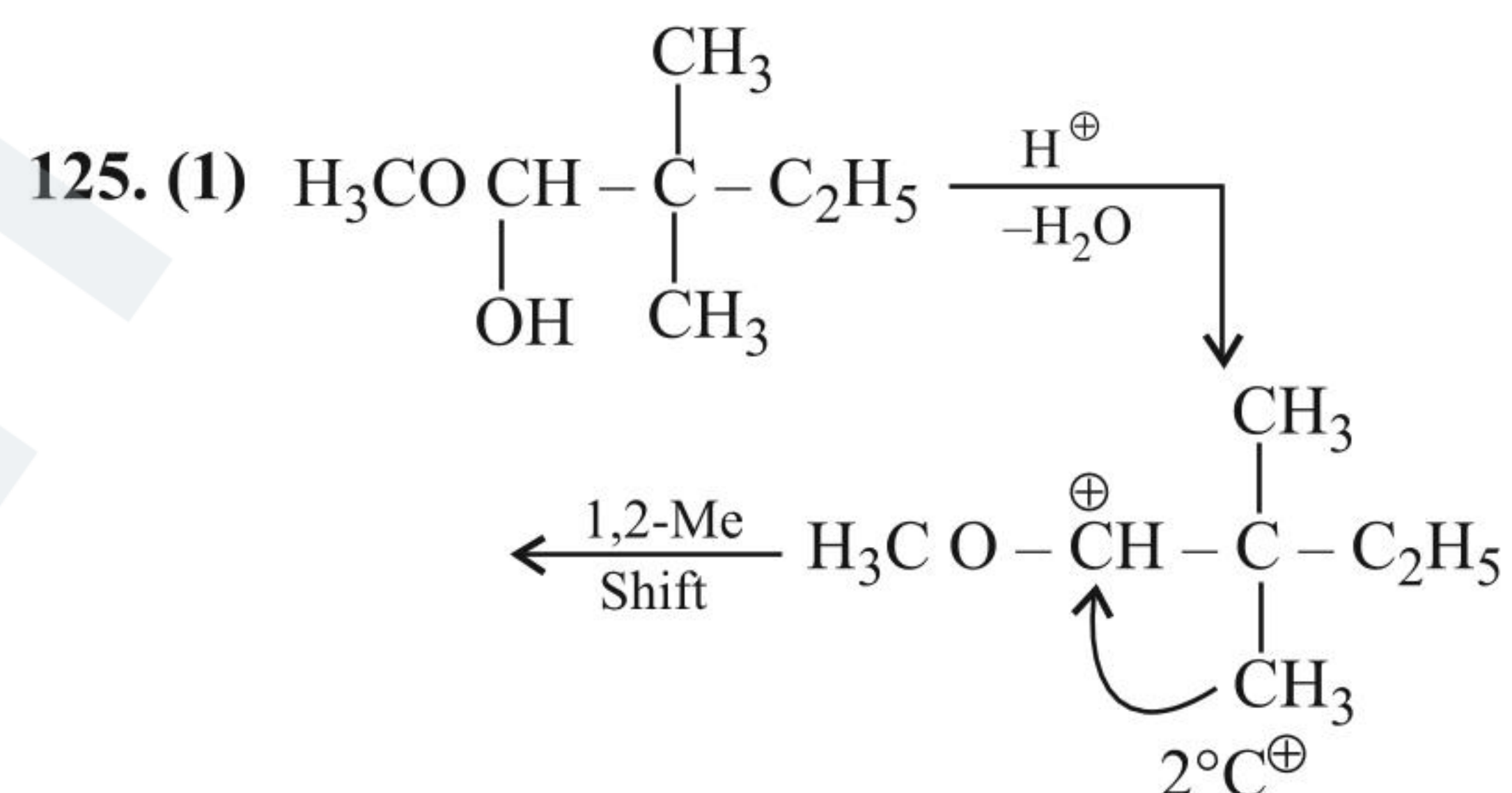
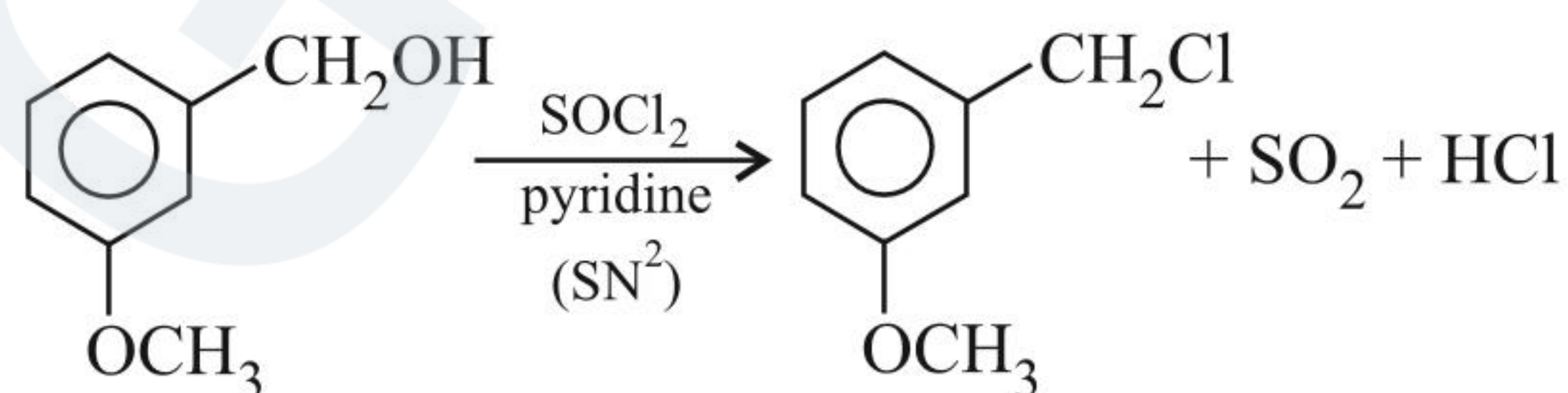


122. (3) Zero DU in compound (A) suggests alcohol or ether. Non-reactivity with Na suggests (A) to be an ether. Iodoform test by (B) suggests the presence of (CH₃—CH—OH) group in B.

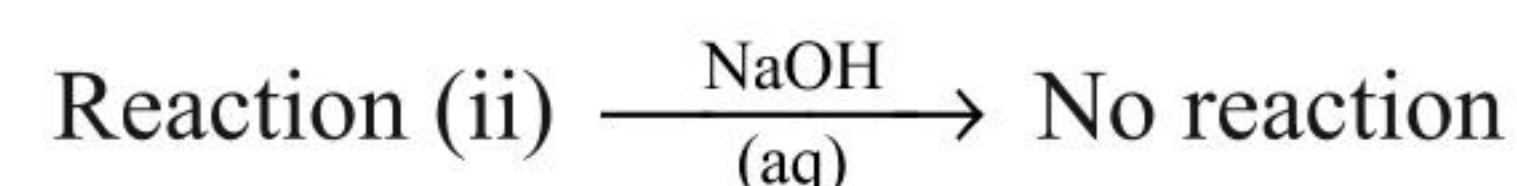
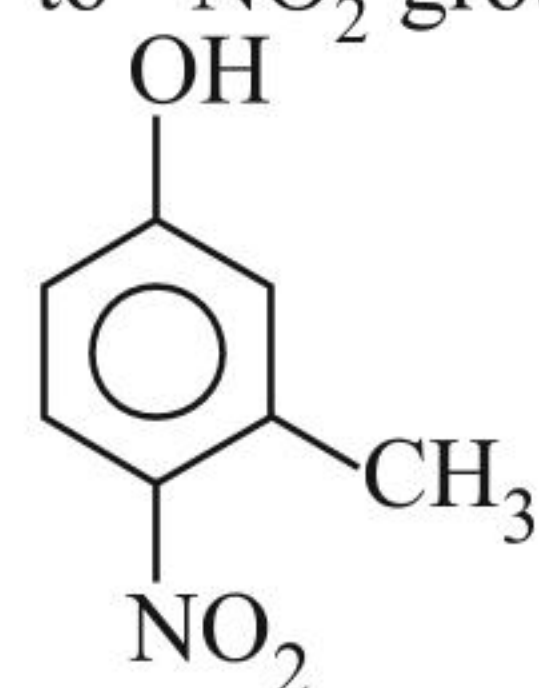


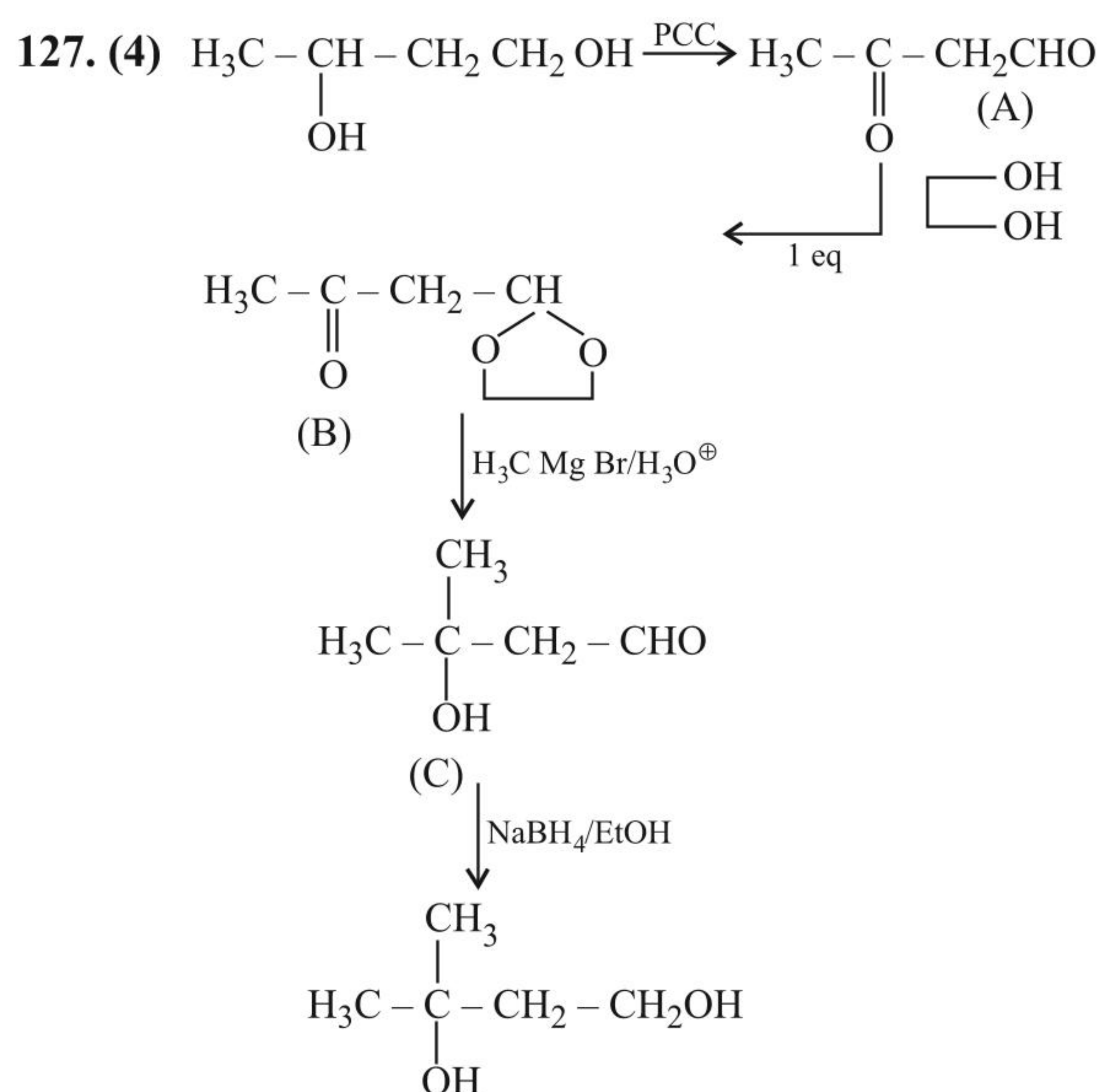
123. (3) In (2) aryl fluoride does not undergo S_N reaction.

124. (1)



126. (3) ArSN reaction is favoured by EWG at *o*- & *p*-positions. In reaction (i), ArSN occurs, due to —NO₂ group (EWG) at *p*-position. In reaction (ii), ArSN reaction does not occur, due to —NO₂ group (EWG) at *m*-position. Reaction (i) $\xrightarrow[\text{(aq)}]{\text{NaOH}}$



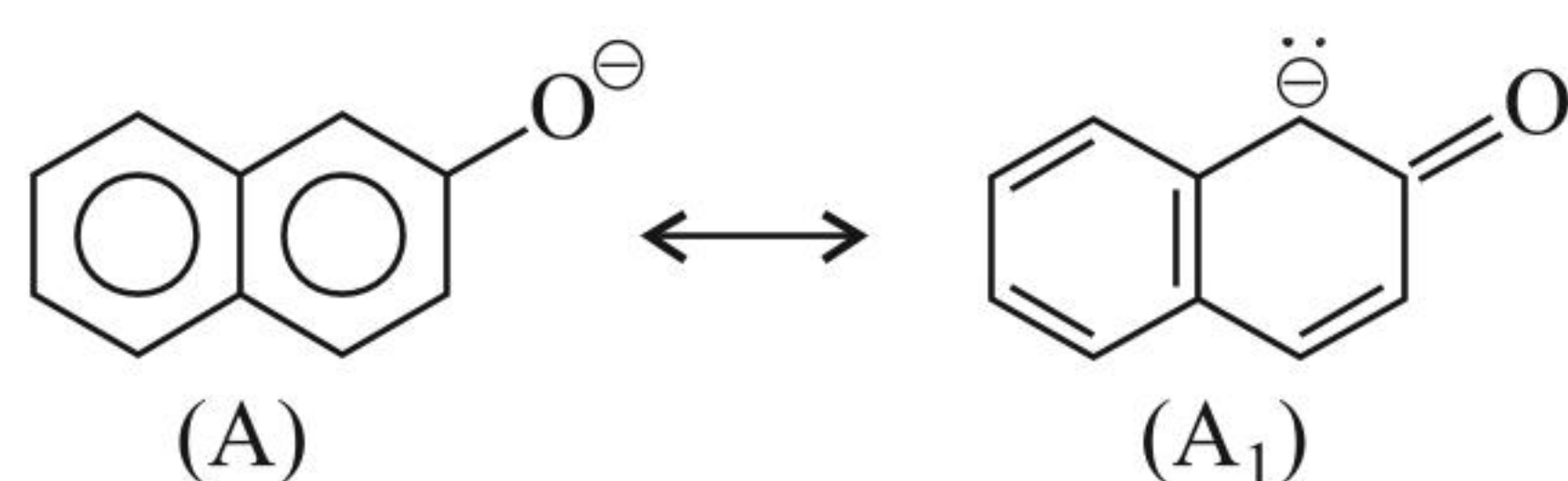


128. (4) Statement (4) is incorrect. Ortho effect operates in substituted benzoic acids and substituted anilines not in substituted phenols. Hence, *o*-methyl phenol is less acidic than phenol.

Multiple Correct Answers Type

1. (1, 4)

The resonance structure of 2-naphthoxide ion (A) is:



(A) is an ambident nucleophile and a better nucleophile than (A₁) because negative charge is on more EN oxygen atom. In the presence of polar non-protic solvent (DMF, dimethyl formamide), O-alkylation is favoured to give product II (C).

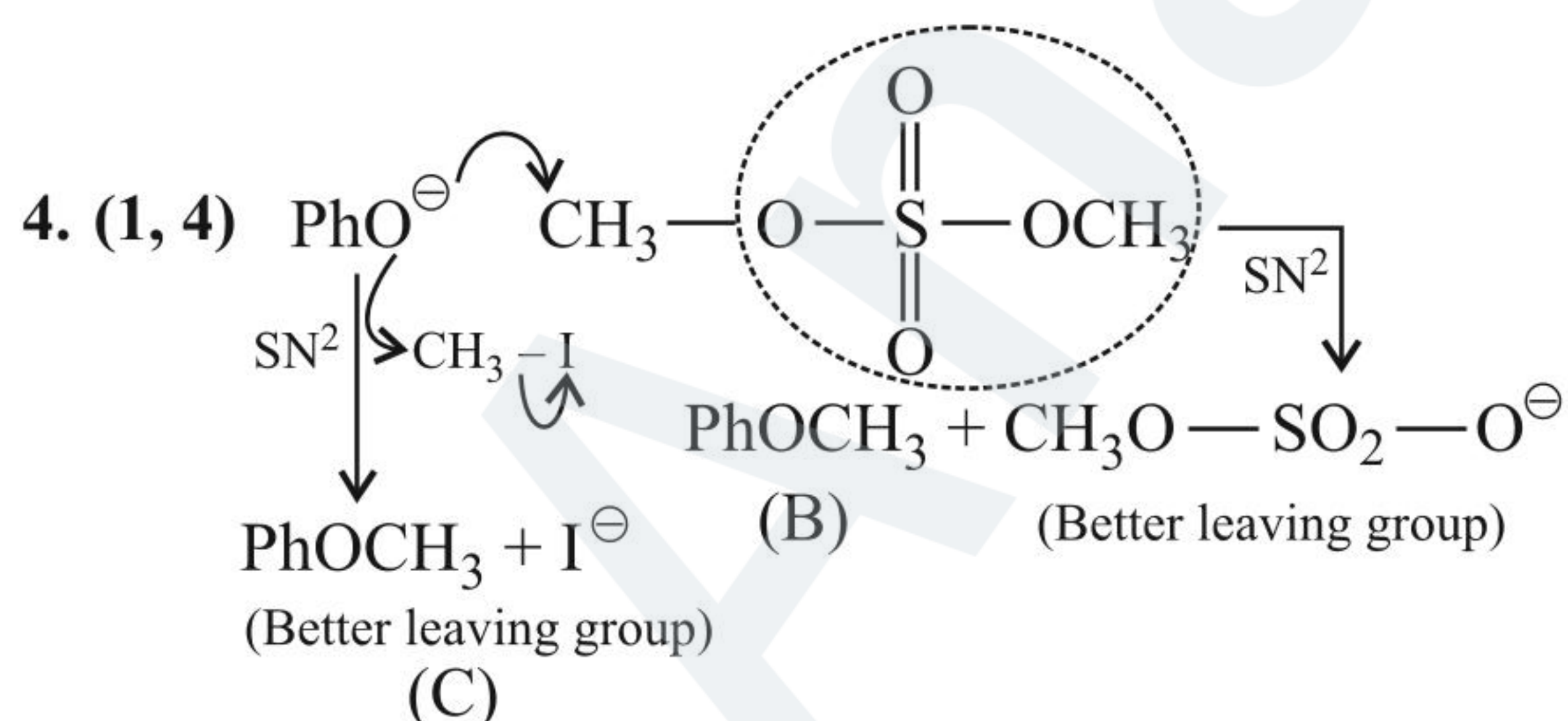
In the presence of protic solvent, hydrogen bonding with the O atom occurs, thus reducing the nucleophilicity of oxygen. Therefore, C-alkylation is favoured to give product I (B).

2. (1, 2, 3, 4)

All statements are self-explanatory.

3. (2, 3, 4)

In (1), the reverse reaction is feasible since phenol is a stronger acid than ethanol.



5. (1, 2, 3, 4)

- Due to -I effect of Cl, 4-chlorophenol is acidic and dissolves in NaOH, but (II) is an aryl halide and does not dissolve.
- (III) is an acid and dissolves in NaHCO₃ but (IV) is a phenol and does not dissolve.
- Although (V) is a phenol, because of the presence of (3NO₂) group, it is exceptionally acidic (pK_a = 0.38). So it dissolves

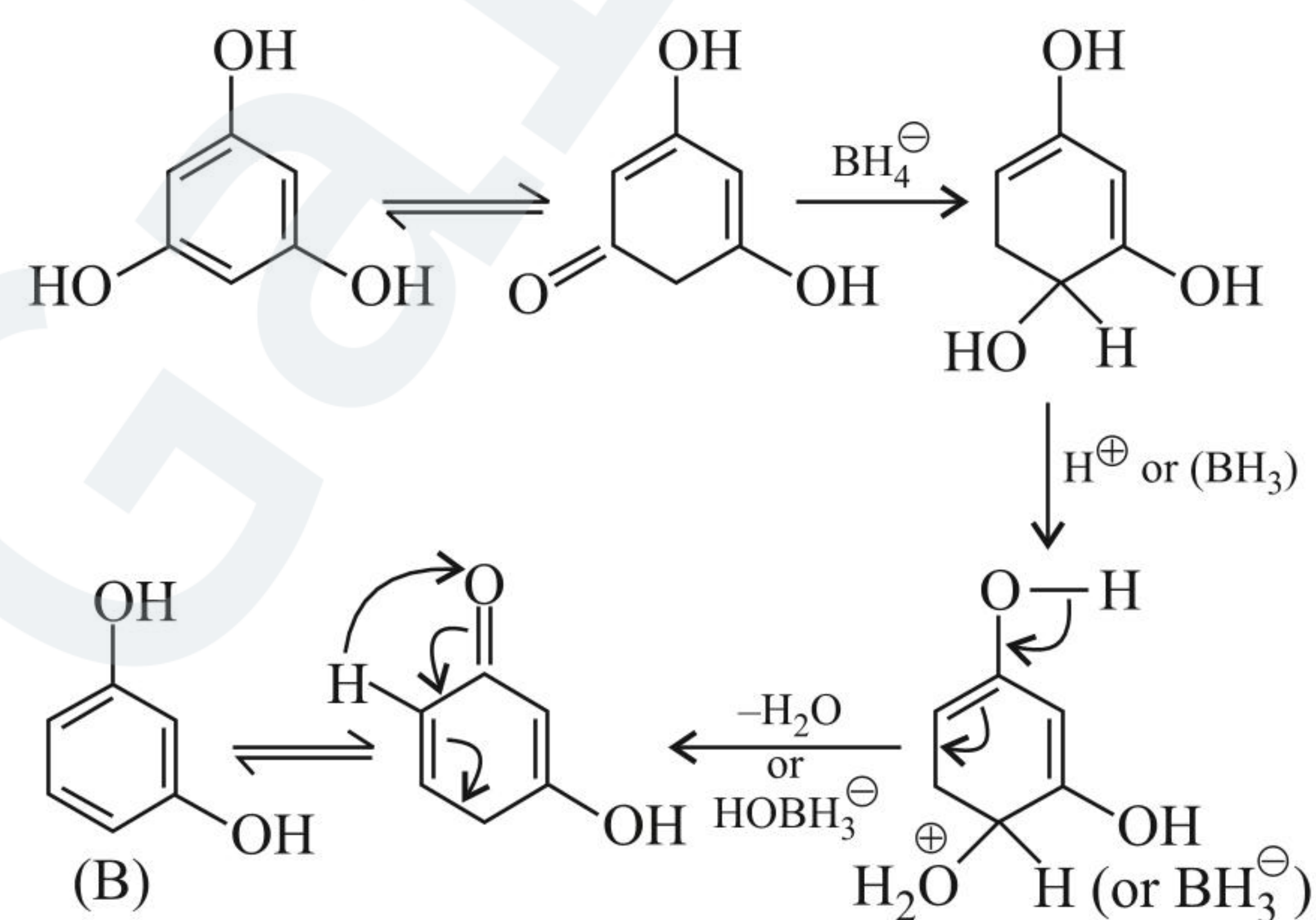
in NaHCO₃, but (VI) is a phenol (pK_a = 10.17) and will not dissolve.

- (4) (VII) is a phenol and dissolves in NaOH, but (VIII) is an ether; and does not dissolve.

6. (1, 2, 4)

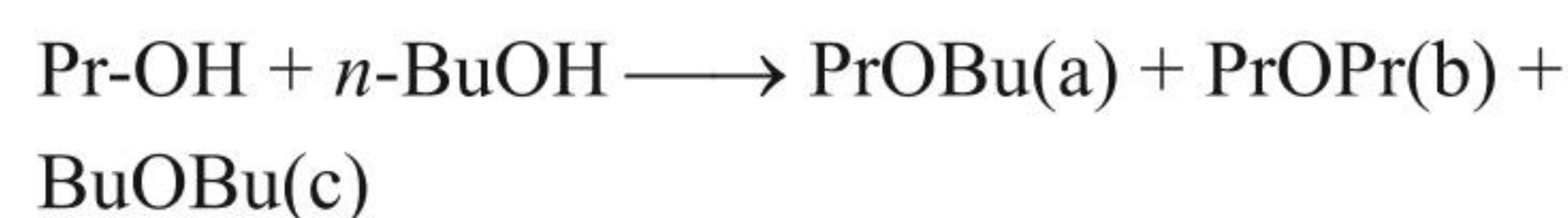
- Ph-O-CH=CH₂ (I), due to the presence of (C=C) bond, reacts with Br₂ by addition (thus, decolourise Br₂ solution) but II does not.
- Due to -I effect of F in (III), it is a stronger acid than (IV) (+I effect of (Me) group).
- Wrong statement.
- Refer to Section 4.10 (c).

7. (3)



8. (1, 2, 3)

A non-symmetrical ether is not usually prepared by heating a mixture of ROH and R'OH in acid. A mixture of three ethers R—O—R, R—O—R', and R'—O—R' is obtained. So the products are:



9. (4)

10. (1)

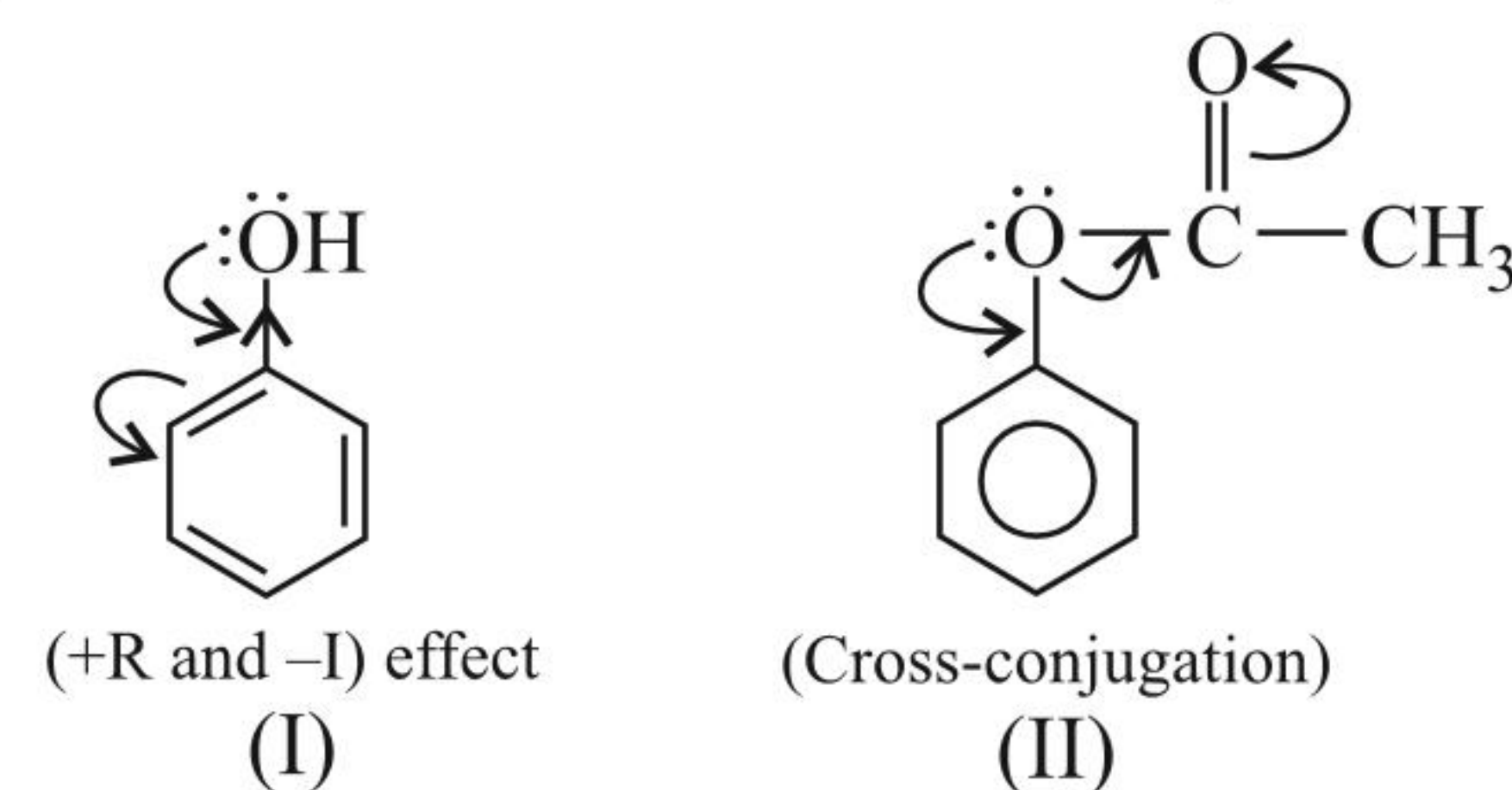
11. (1, 3, 4)

12. (2, 3, 4)

13. (1, 3)

14. (1, 2, 3, 4)

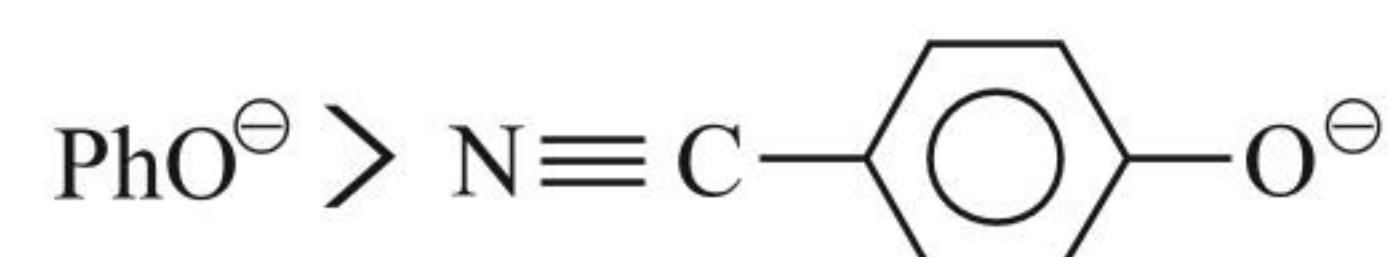
- (1) Correct. SE reaction is favoured by EDG; less favoured by EWG.



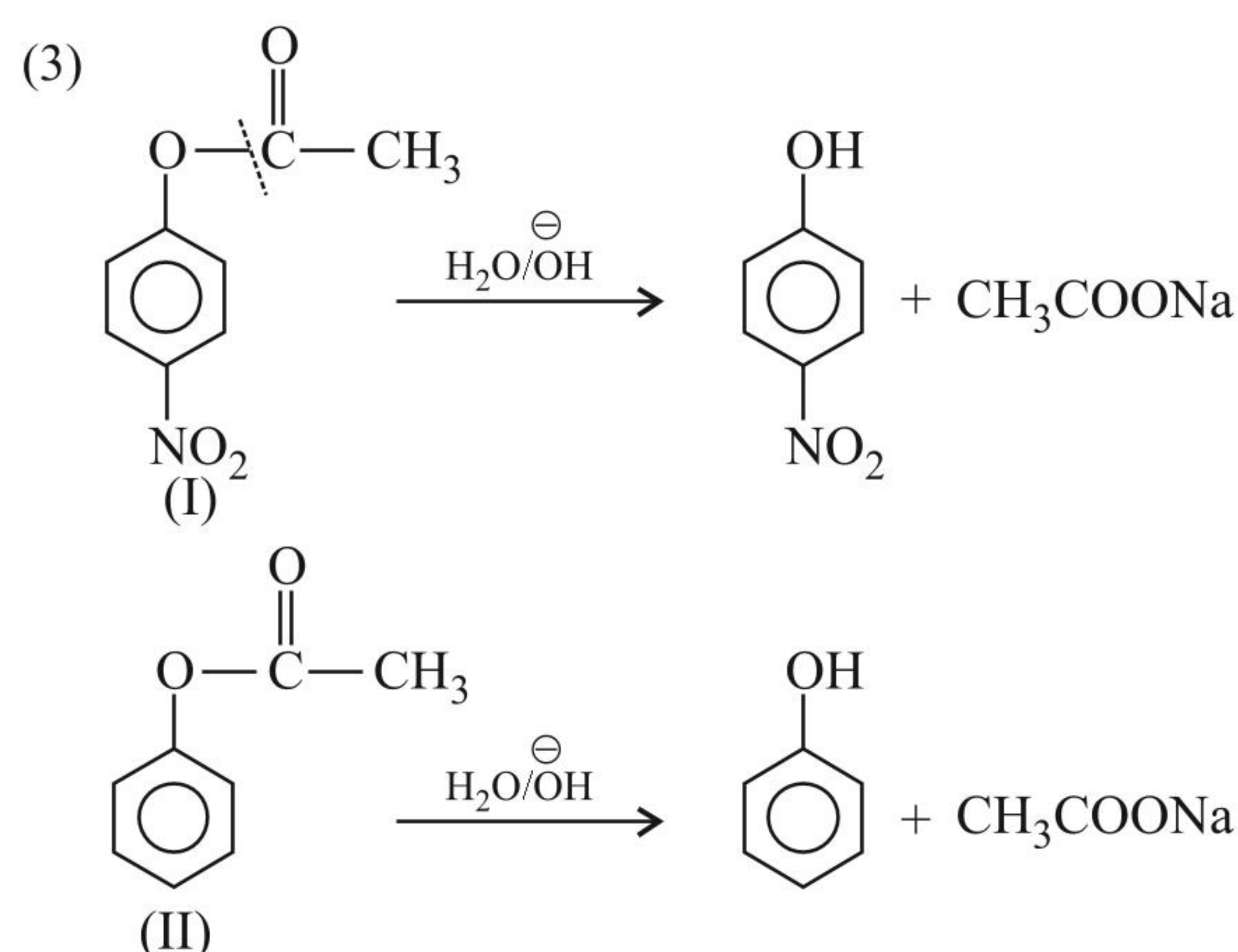
Due to cross-conjugation in (II), \bar{e} -donating power of oxygen to the ring decreases and hence it is less reactive than (I).

- (2) Acidic character: $\text{N}\equiv\text{C}-\text{C}_6\text{H}_4-\text{OH} > \text{PhOH}$
- Due to EW (CN) group

Basic and nucleophilic character:



Since, PhO^- is a stronger nucleophile than $p\text{-NC-C}_6\text{H}_4\text{O}^-$. Hence, it reacts faster with PhCH_2Cl .



As we know, (I) is faster than (II). The \bar{e} -withdrawing effect of (p -NO₂) group ($-R$ and $-I$), from O makes p -NO₂—C₆H₄—O[⊖] a weaker base and better leaving group.

(4) Esterification of PhOH is faster than p -nitrophenol. Phenol, a less acidic compound (or more basic) is more reactive in acidic conditions. With its \bar{e} -withdrawing (p -NO₂) group, p -nitrophenol is less basic and less reactive.

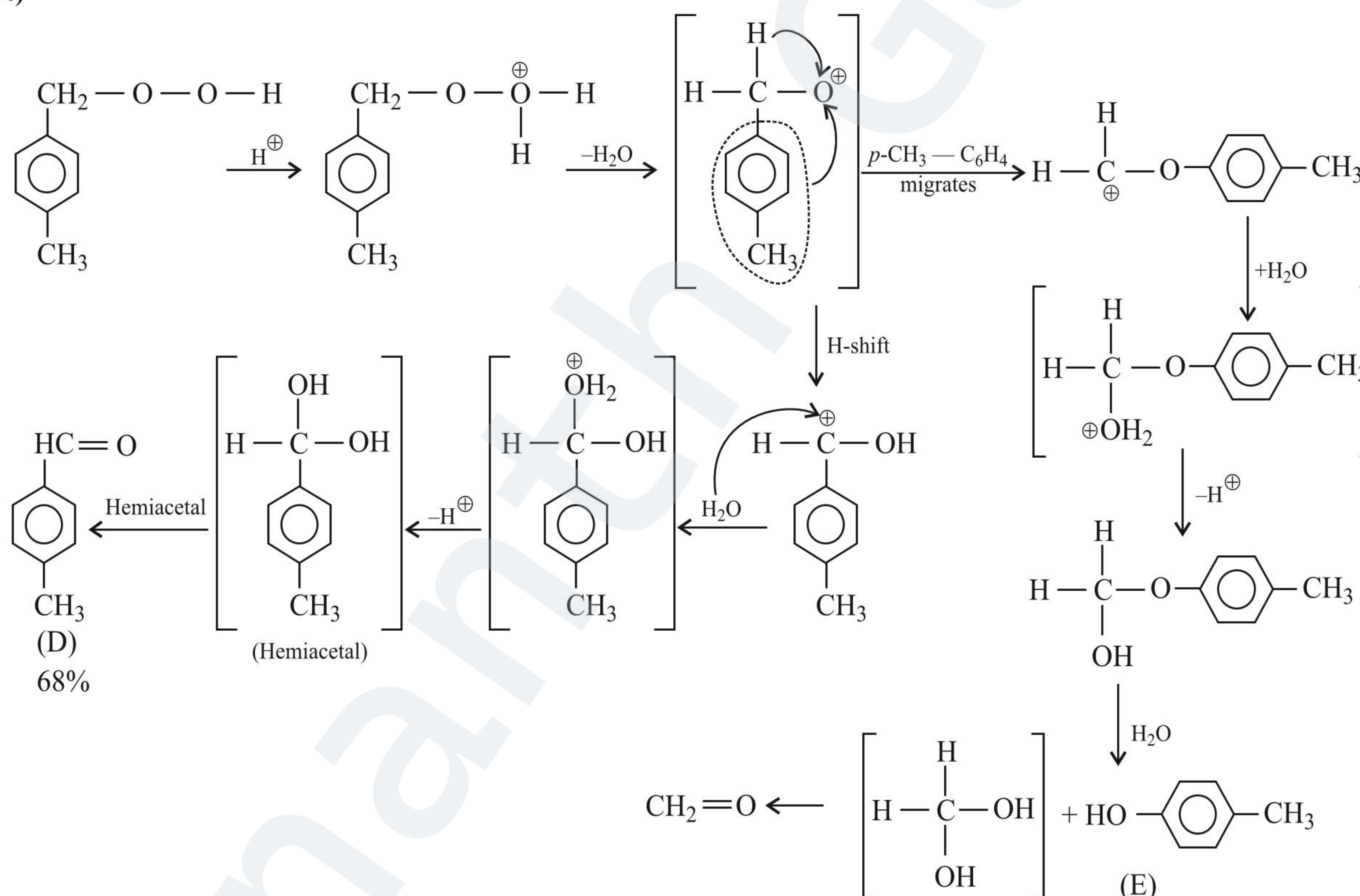
15. (1, 2, 3)

- (1) PhOH has higher boiling point due to H-bonding.
- (2) Molecules of p -benzonoquinone can fit closer in solid state causing it to have higher melting point.
- (3) and (4)

Intramolecular H-bonding (chelation) in the o -isomers inhibits the intermolecular attraction, lowers the boiling point, reduces H-bonding with H₂O, and decreases water solubilities. Intra-molecular chelation does not occur in m - and p -isomers.

16. (2, 4)

17. (1, 3, 4)



The yield of (D) is greater than (E) because H is a better migrator than the Ar-group. Moreover, there are 2H and one Ar-group, so statistically the yield of (D) is about twice that of (E).

18. (1, 3)

Even in the presence of two (Me) groups, (Ph) group is a better migrator than (Me) group.

19. (1, 2, 4)

- (1) The \bar{e} -donating effect of (OH) makes the ring of phenol very \bar{e} -rich, enabling it to readily donate \bar{e} 's to oxidising agents.
- (2) Benzaldehyde reacts with NaHSO₃ but PhCl does not.
- (3) Both react with NaOH to form sodium salts.
- (4) Dry ice (CO₂) reacts with aq. NaOH to form NaHCO₃, which reacts with acid to form PhCOONa + CO₂ + H₂O.

20. (1, 2, 3, 4)

- i. Although o -nitrophenol should be more acidic than p -nitrophenol, but due to intramolecular H-bonding it is less acidic.
- ii. There is only $-I$ effect of (NO₂) group at m -position, so (b) is less acidic than (I) ($-R$ and $-I$ at $para$).
- iii. Phenol is less acidic than (I) ($-R$ and $-I$).
- iv. p -Cresol is less acidic ($+I$ and H.C. effects) of (Me) group than I ($-R$ and $-I$).

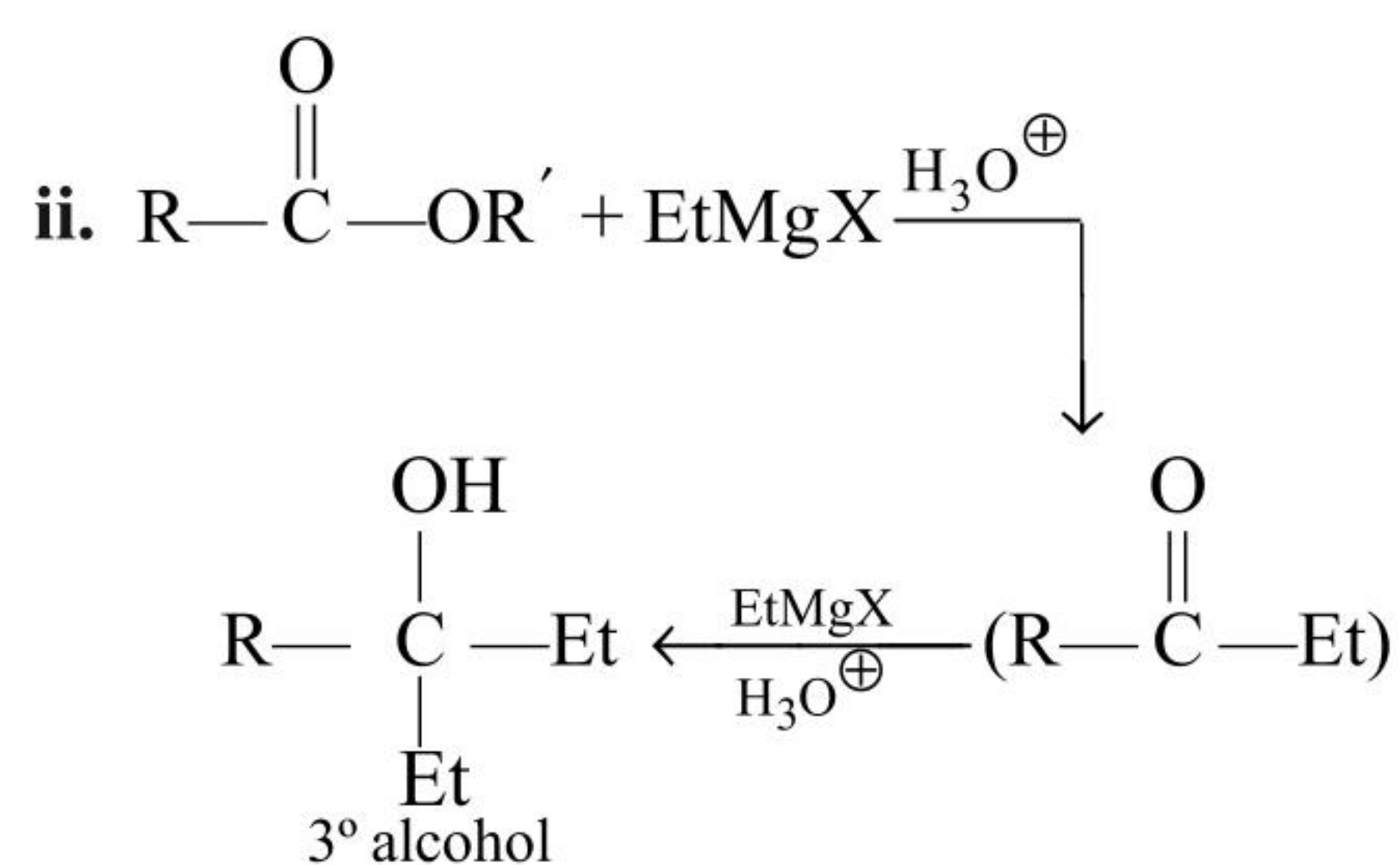
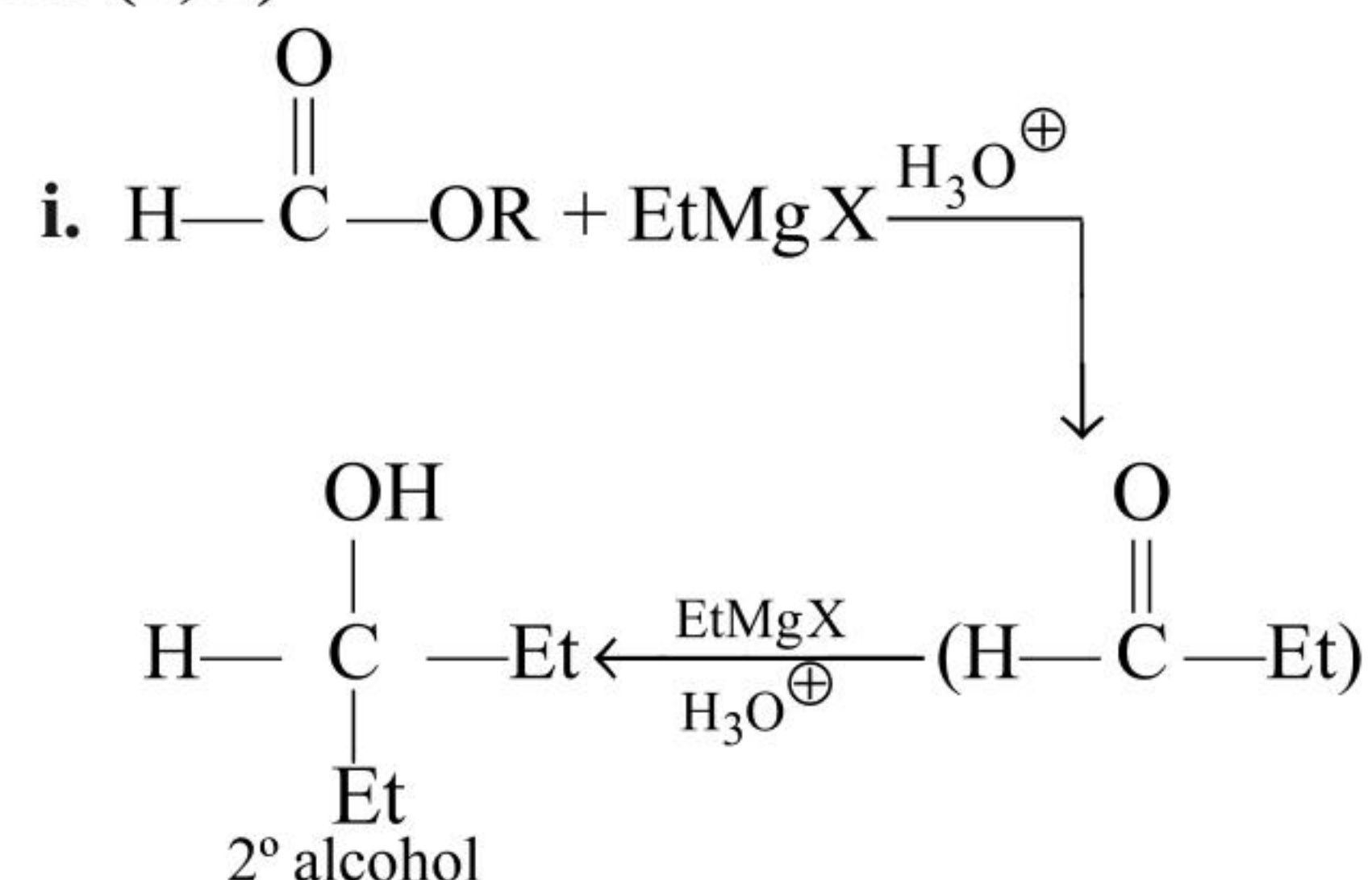
21. (1, 3, 4)

Cl_2 oxidises alcohols to aldehyde and ketones but does not convert them into RCl .

22. (2, 3, 4)

Reaction (1) is not feasible since the ring is not activated by EWG (e.g., NO_2 group). So, ArSN reaction is not feasible.

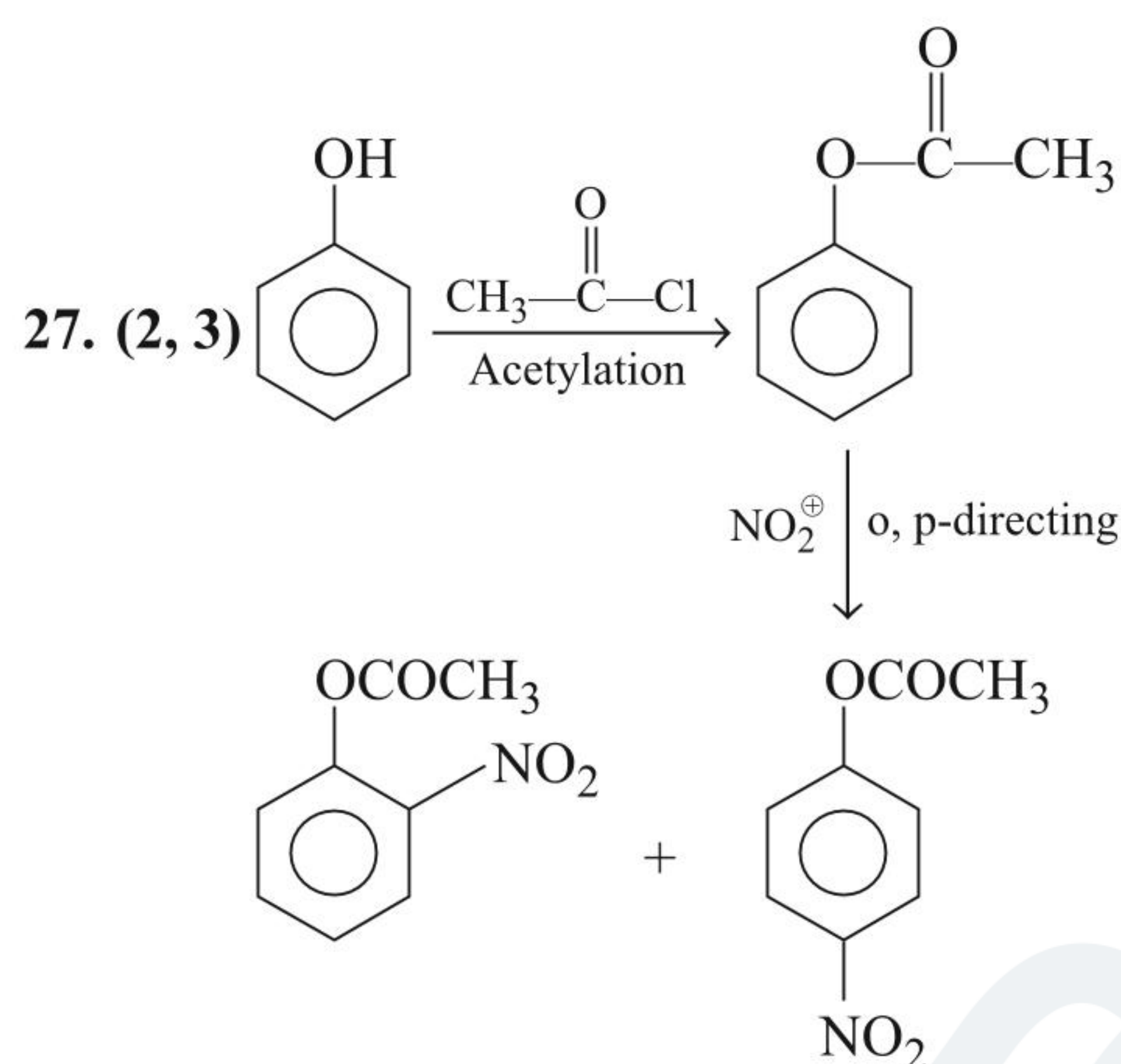
23. (2, 3)



24. (1)

25. (1, 2, 3)

26. (2, 3)



28. (1, 2, 3, 4)

NaHCO_3 cannot react with phenol and less acidic than phenol.

29. (3, 4)

Lucas reagent and $\text{K}_2\text{Cr}_2\text{O}_7$ can differentiate 2° alcohol (A) and 1° alcohol (B).

30. (1, 2)

For Reimer-Tiemann reaction, ring must have activating group (i.e., EDG).

31. (1, 2)

Ring expansion take place when carbocation is out side of three/four/five membered ring.

32. (1, 2, 3)

Consider acid-base reaction.

33. (1, 2, 3)

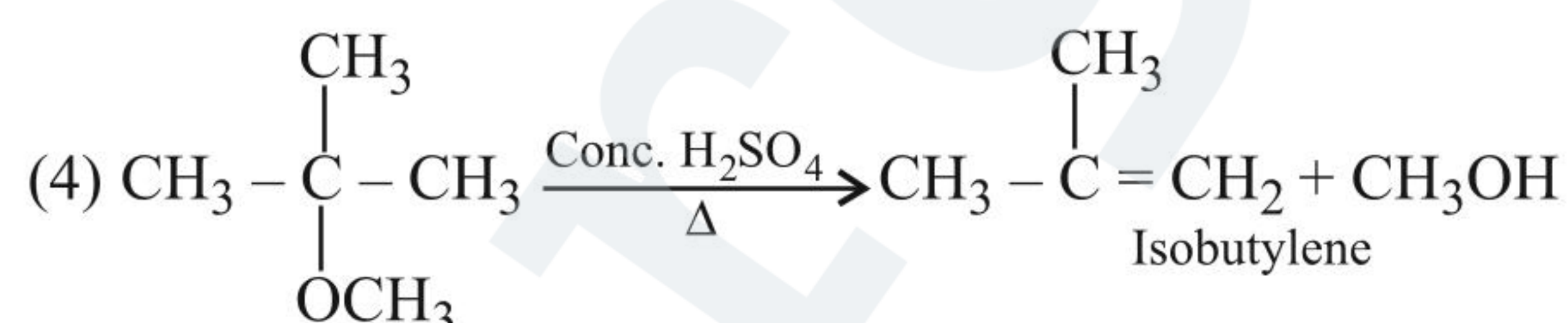
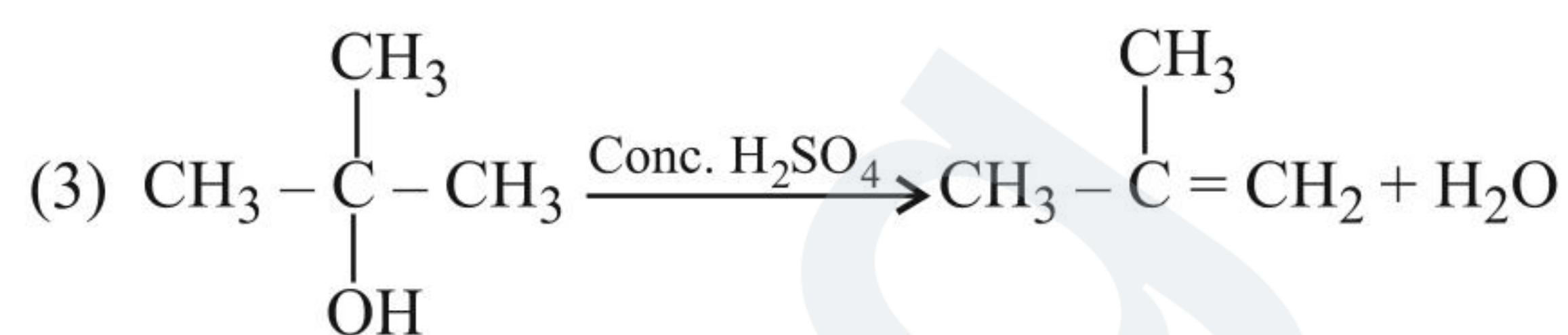
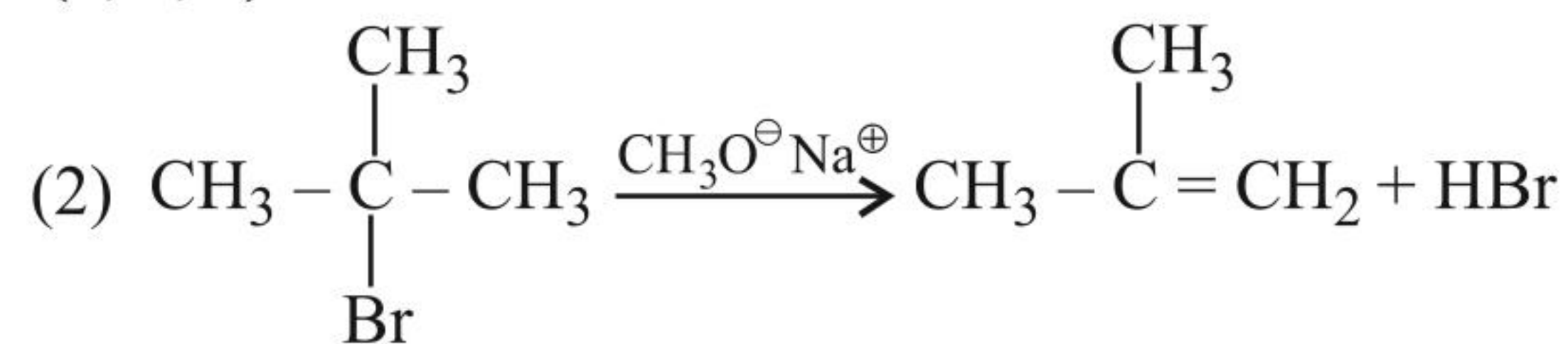
Consider stability of conjugate base or pK_a value

Acidic order $\Rightarrow \text{MeOH} > \text{H}_2\text{O} > \text{ROH} > \text{R}-\text{C}\equiv\text{CH}$

34. (1, 2, 4)

Acidic of *o*-nitrophenol is minimum due to intramolecular H-bonding.

35. (2, 3, 4)



36. (2, 3, 4)

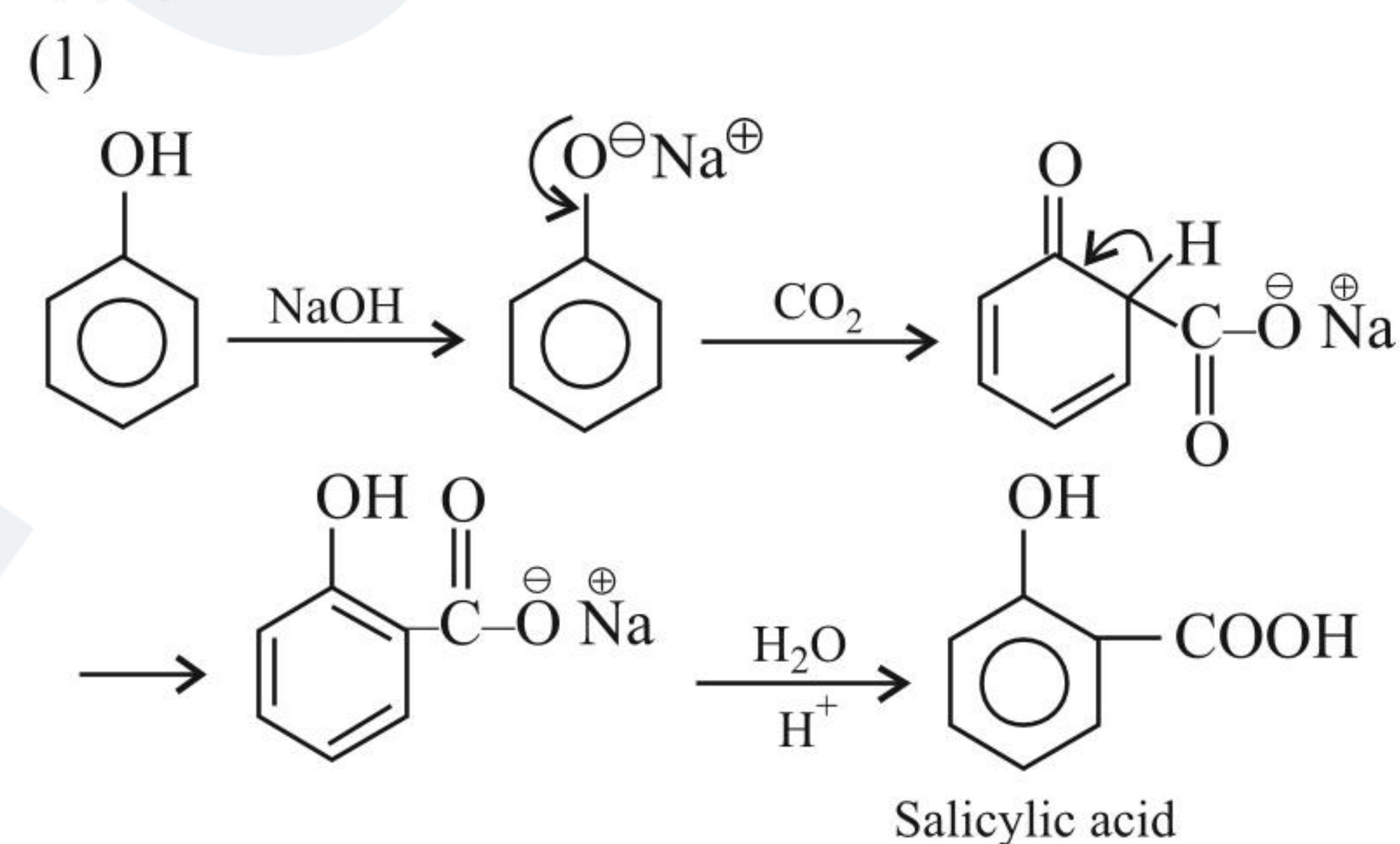
In esterification reaction

i. $-\text{OH}$ of $\text{R}-\text{COOH}$ is replaced by $\text{R}'\text{O}$ of ROH

ii. $\text{R}'\text{OH}$ acts as nucleophile and attacks on $-\text{CO}-$ of $\text{R}-\text{COOH}$

iii. Larger is the size of R group, lesser the rate of esterification

37. (1, 2)



38. (1, 2)

39. (1)

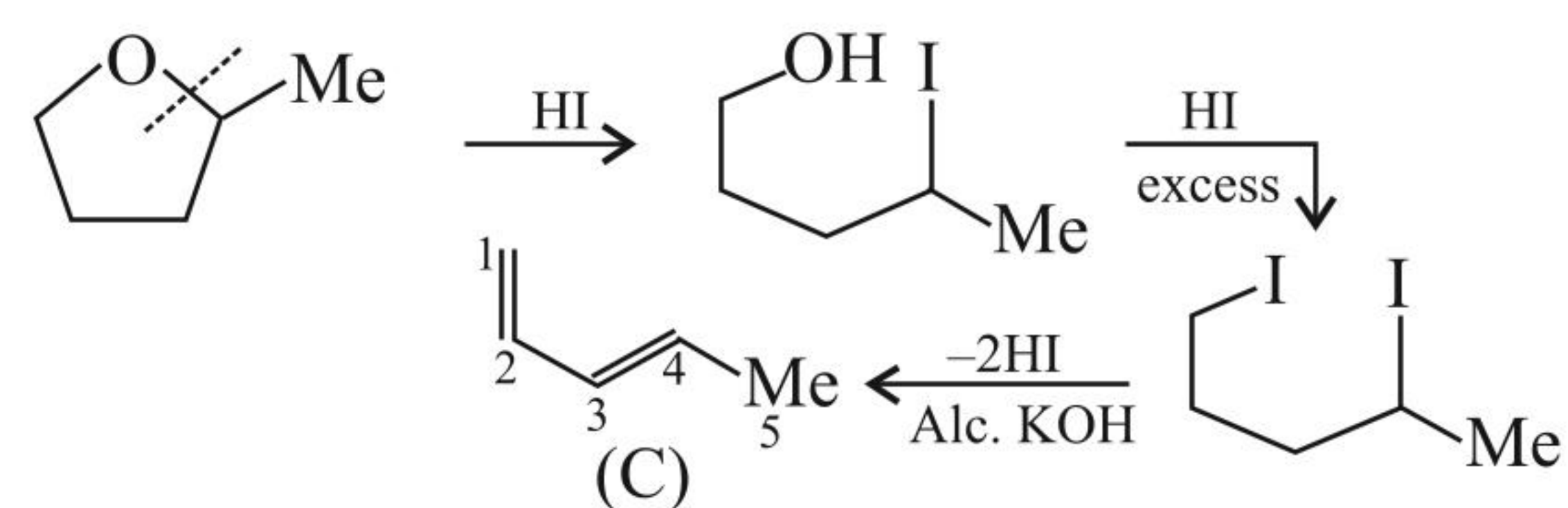
40. (1, 4)

41. (2, 4)

42. (4)

43. (3)

44. (1) One DU in (A) and formation of (B) with two I atoms suggest that (A) is a ring. The formation of (C) (five C atoms) suggest that (A) is a five-membered ring ether. So (A) is (a).



45. (1, 2)

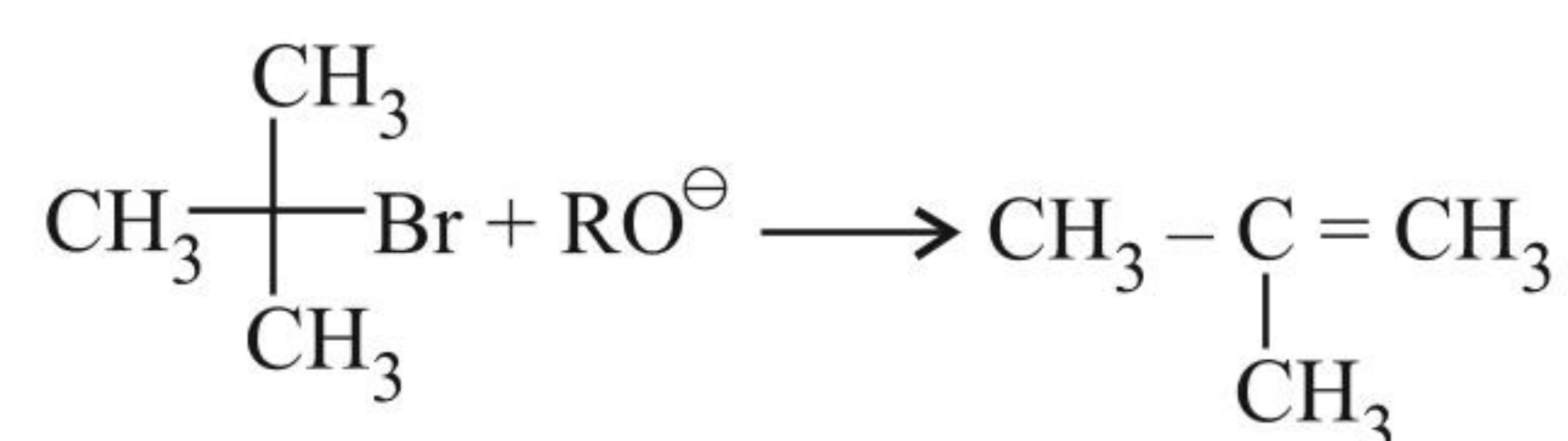
46. (1, 2)

47. (3, 4)

(1) gives elimination product. (2) is not possible as aryl halides do not undergo substitution easily.

48. (2, 4)

Correct product for (2) option.

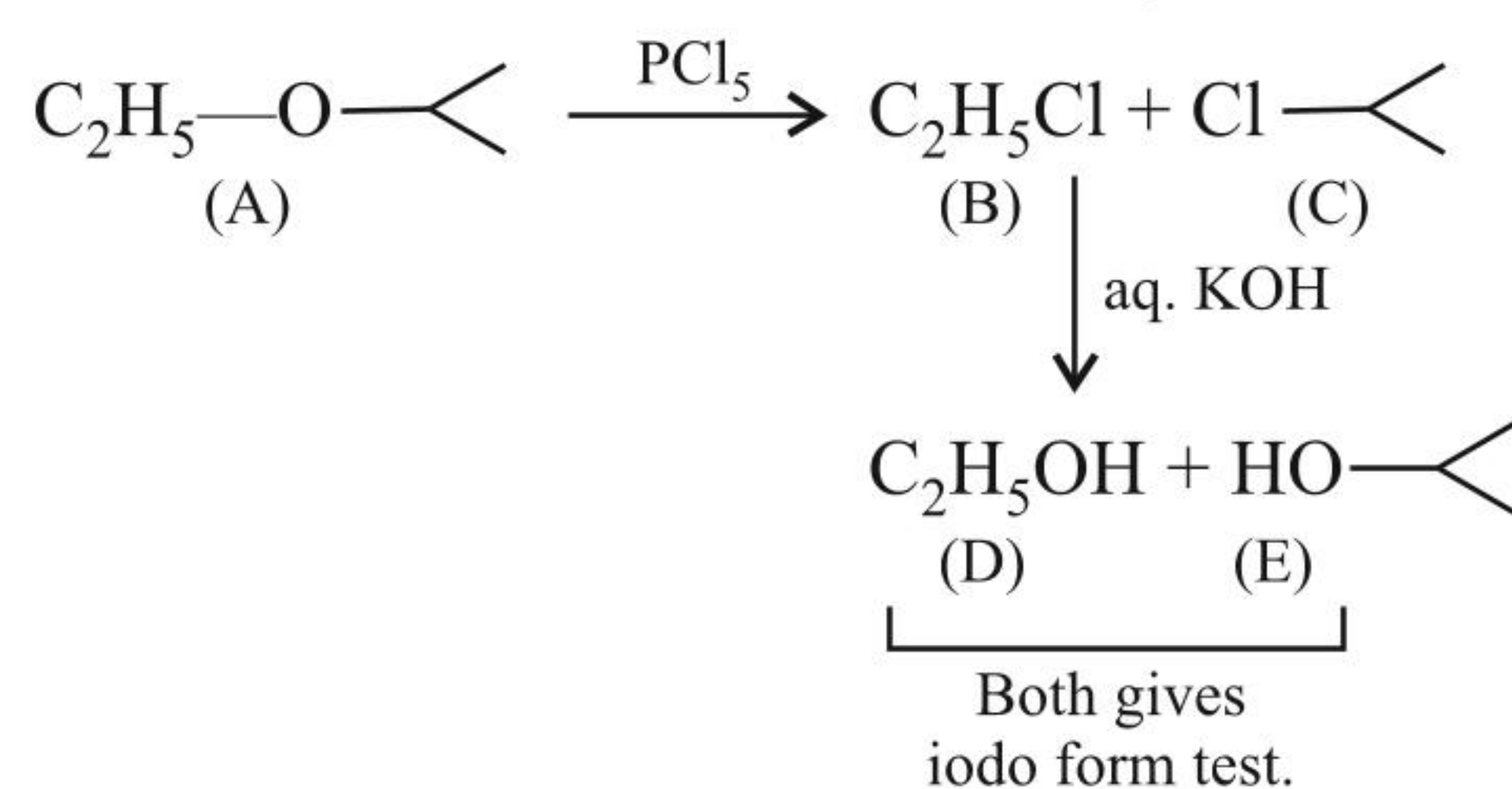


Option (4) is also not feasible because aromatic halide do not given S_N reaction in normal condition.

49. (1, 4)

50. (1, 3, 4)

Ether must contain alkyl group whose alcohol should give iodo form test, *i.e.*, isopropyl group and C_2H_5 group.



51. (1, 2, 4)

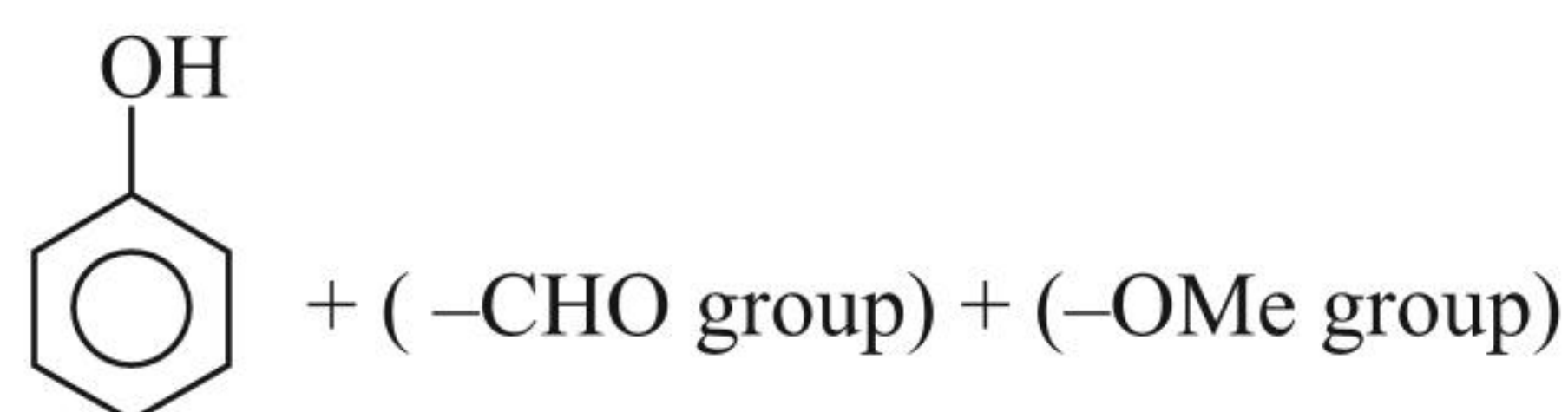
- (1) Fries rearrangement
- (2) Claisen rearrangement
- (4) Ring extension.

Linked Comprehension Type

Paragraph 1

1. (2) 2. (1) 3. (3) 4. (1) 5. (3)

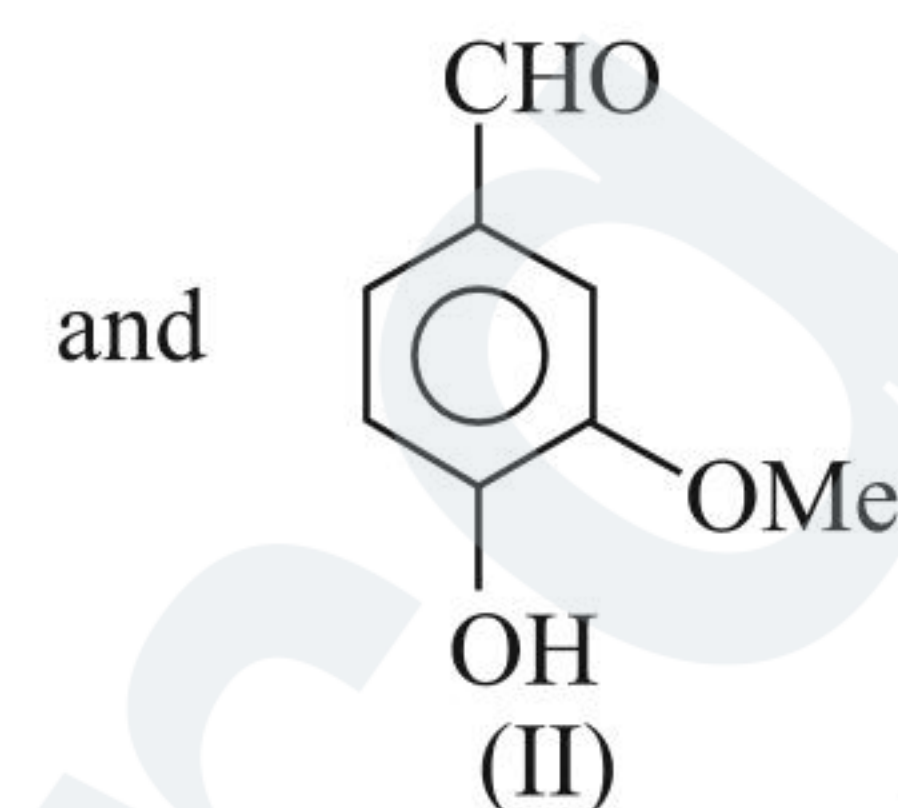
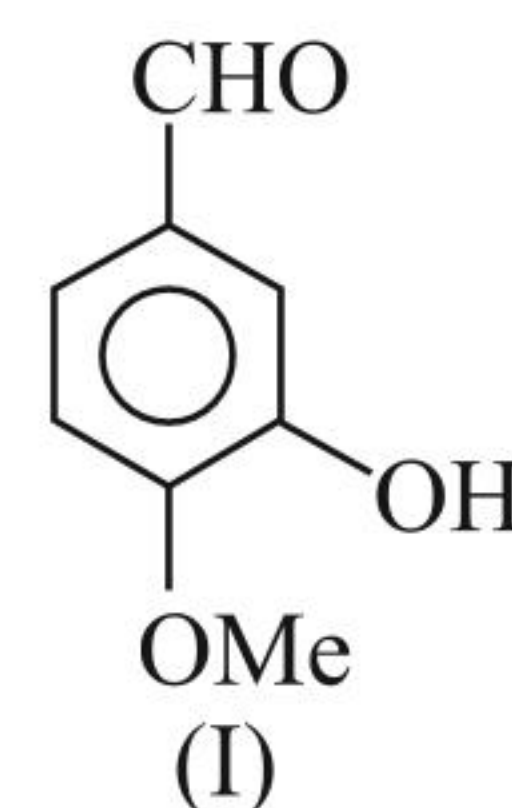
- i. (A) gives colour with $FeCl_3$, suggesting phenolic group.
- ii. (A) gives positive Tollens reagent test, suggesting ($-CHO$) group.
- iii. (A) contains only one ($-OH$) group, since it reacts with 1 mol of CH_3I to form mono methyl ether.
- iv. (A) is not steam distilled, which suggests that ($-OH$) and ($-CHO$) groups are not in *o*-position.
- v. Total C atom and O atom, 6C (benzene) + $-CHO$ + ($-OH$) group.
- vi. Formula of (A) = $C_8H_8O_3$
- vii. To count for one additional C atom and one additional O atom, ($-OCH_3$) group must be present in (A).
- viii. A must contain



and ($-OH$) and ($-CHO$) not in *ortho*-position.

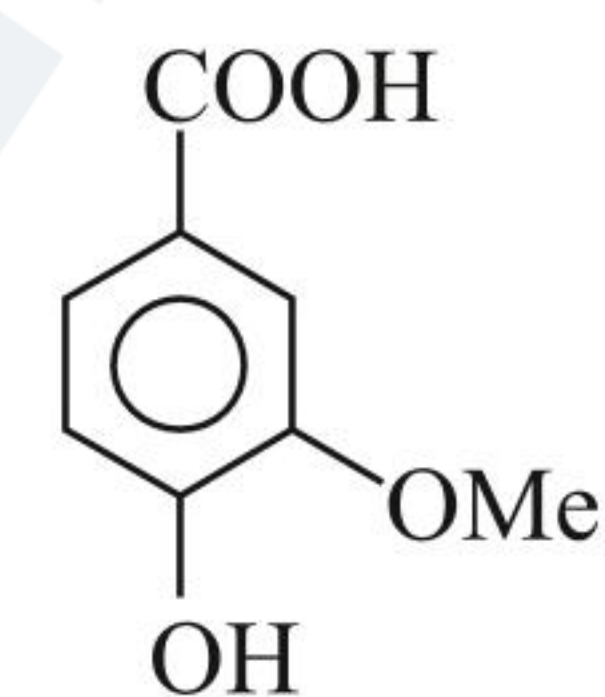
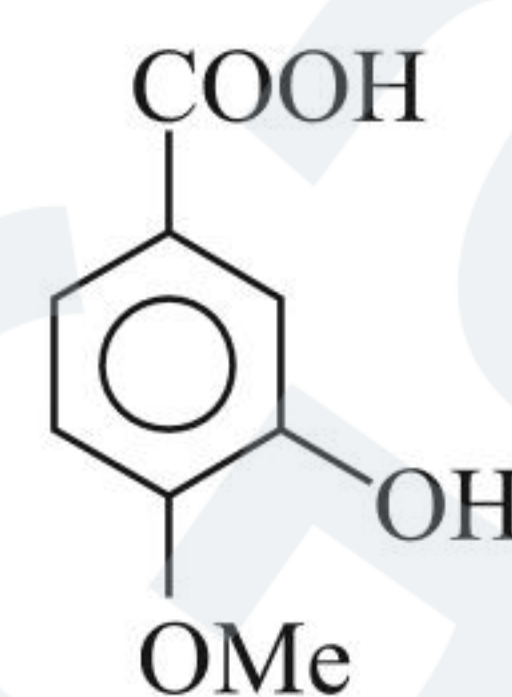
ix. Formation of (D), ; suggests two possible structures of

(A):



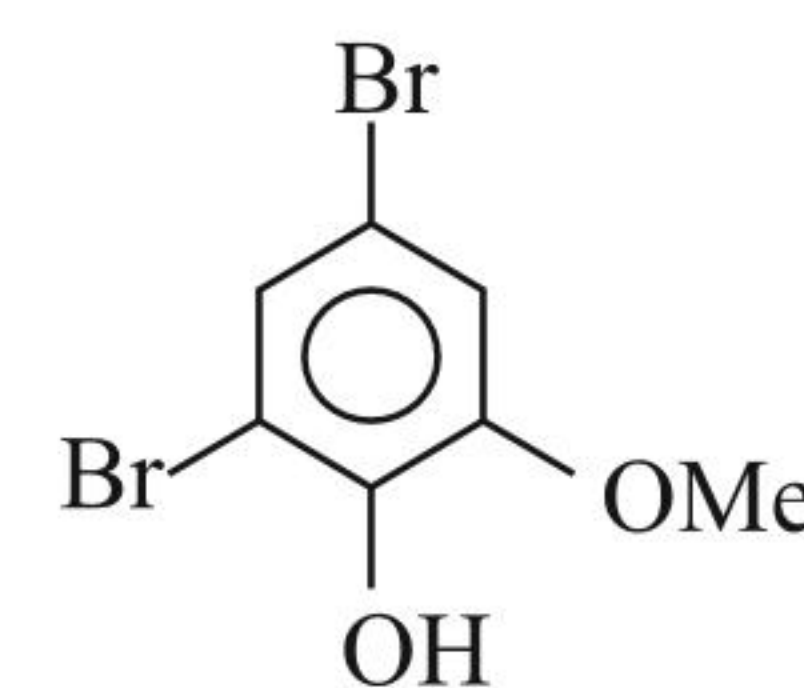
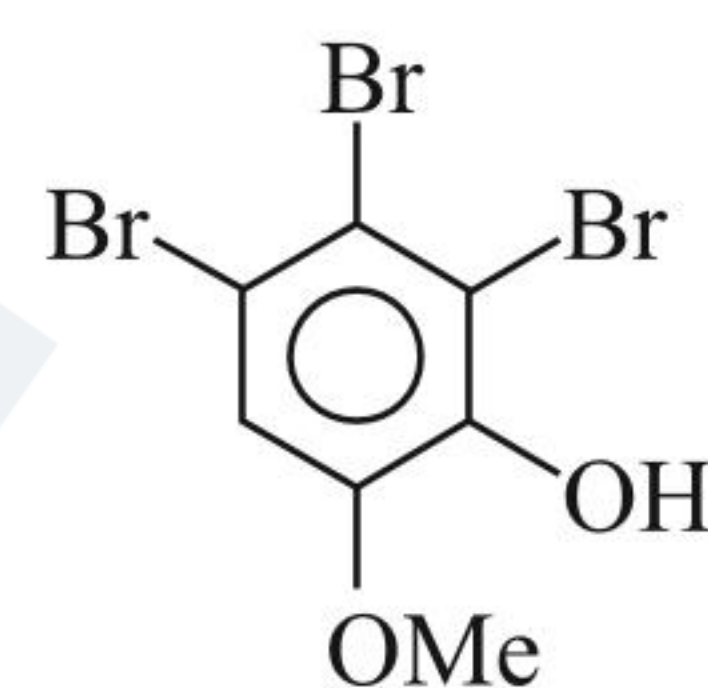
↓ Tollens test

↓ Tollens test



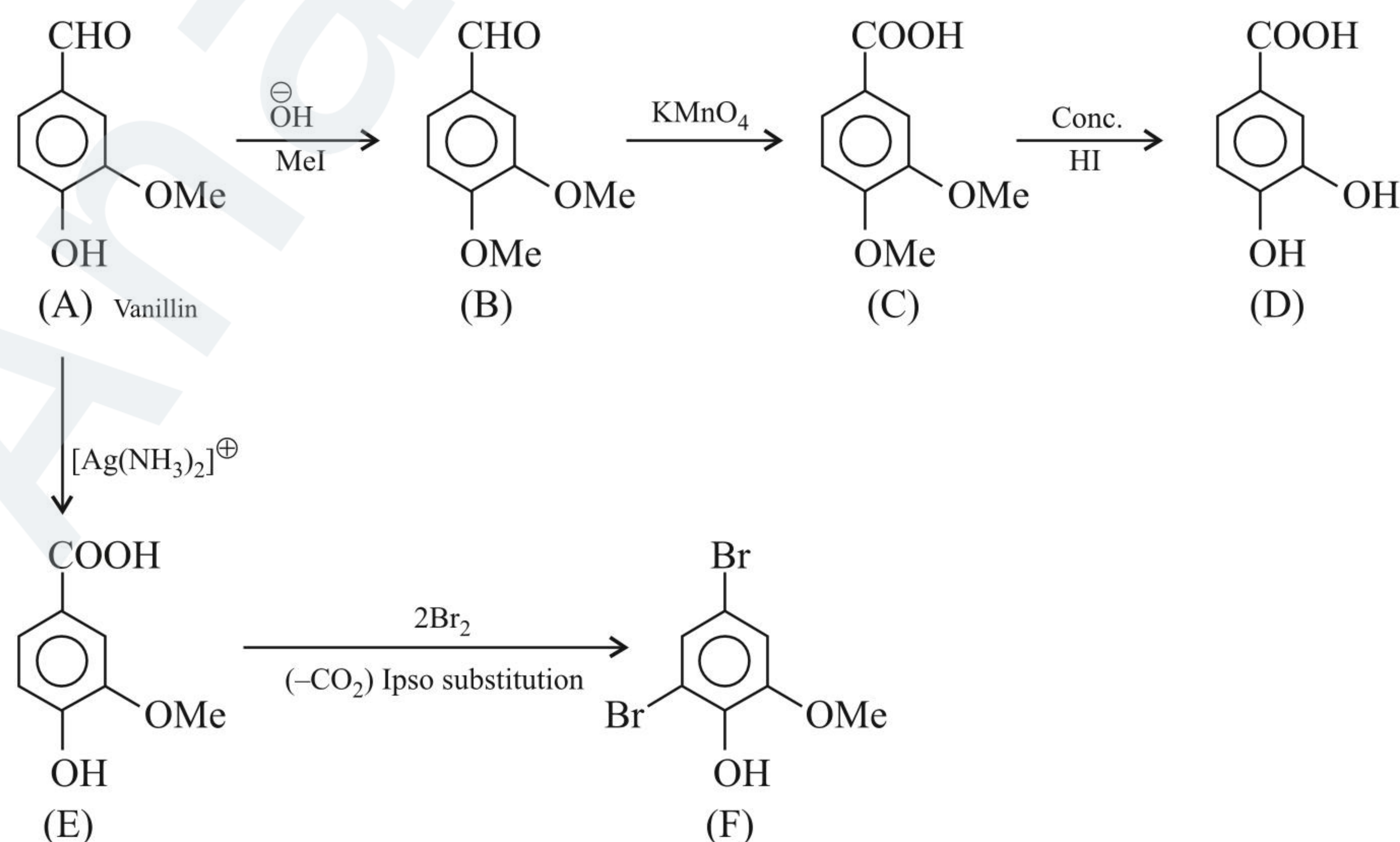
↓ $-CO_2$ Br_2

↓ Br_2 $-CO_2$ (Ipsso substitution)



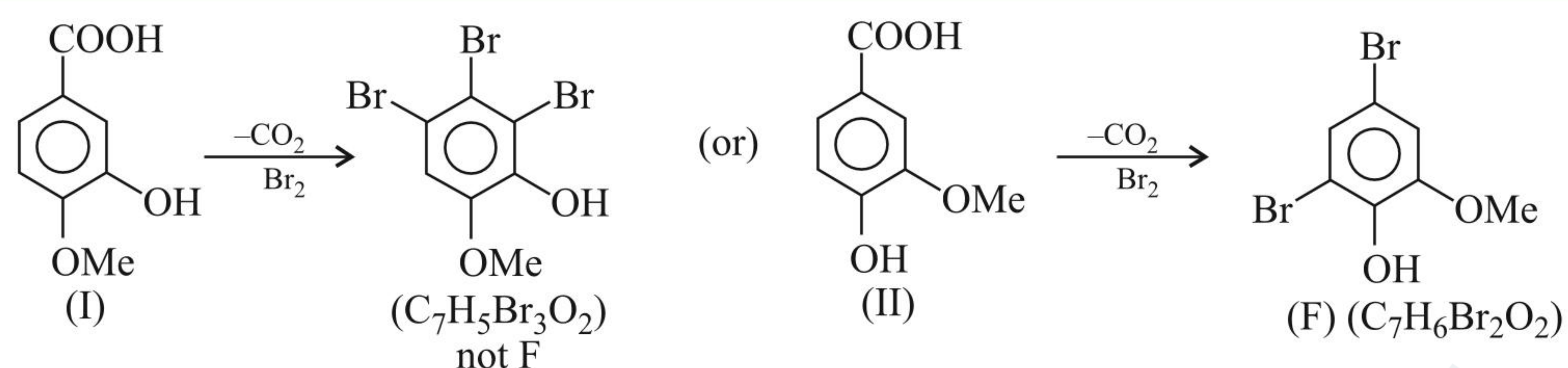
But the compound $F(C_7H_6Br_2O_2)$ contains Br_2 , which is only possible with compound (II). Therefore, structure (A) is (II).

Reactions:



Alternative method of solving the problem:

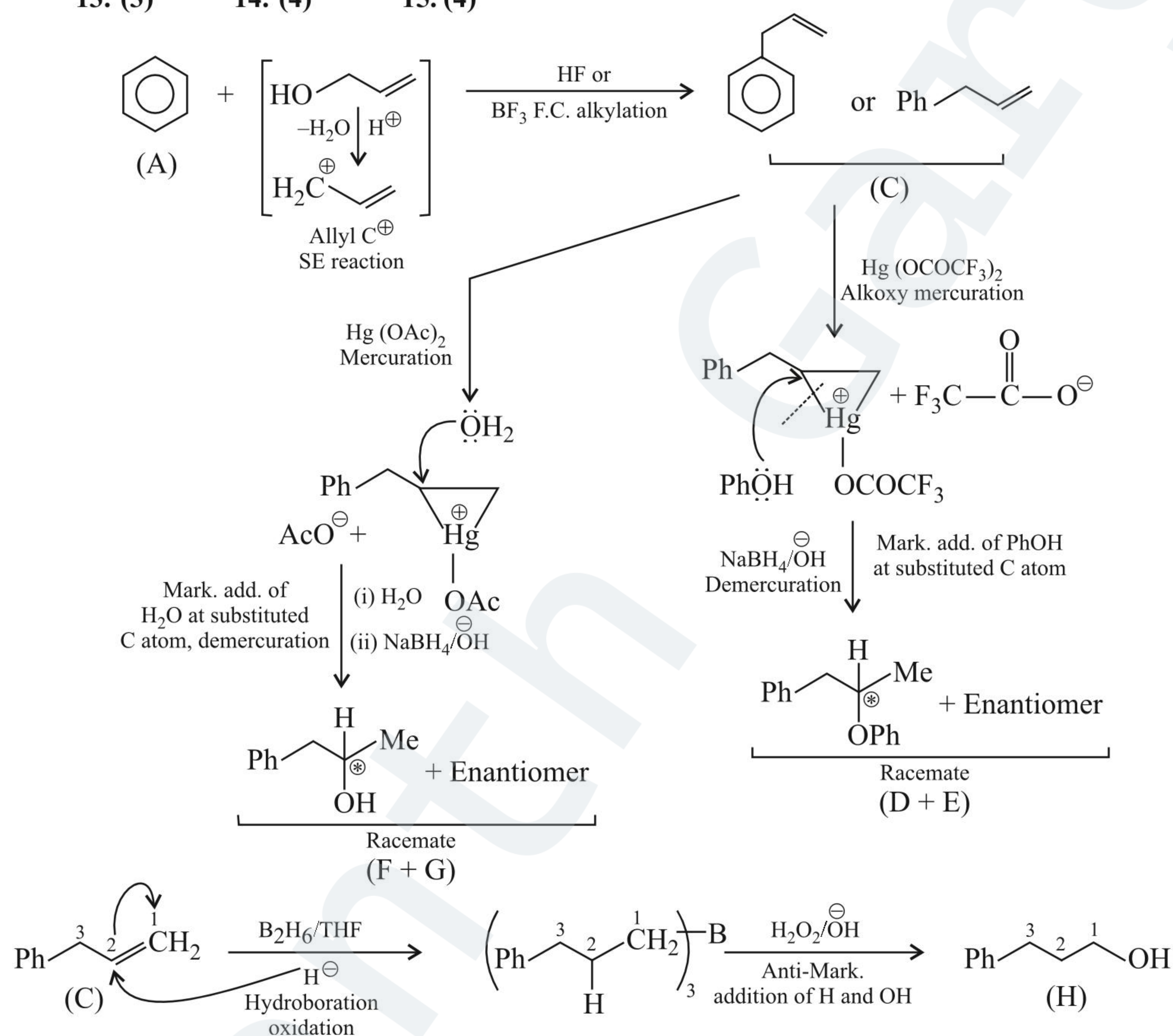
Start from (D) and proceed reverse to (C). (D) is obtained from (C) by HI, so two structures are possible for (A).



So, (A) is II and then proceed to find out other products.

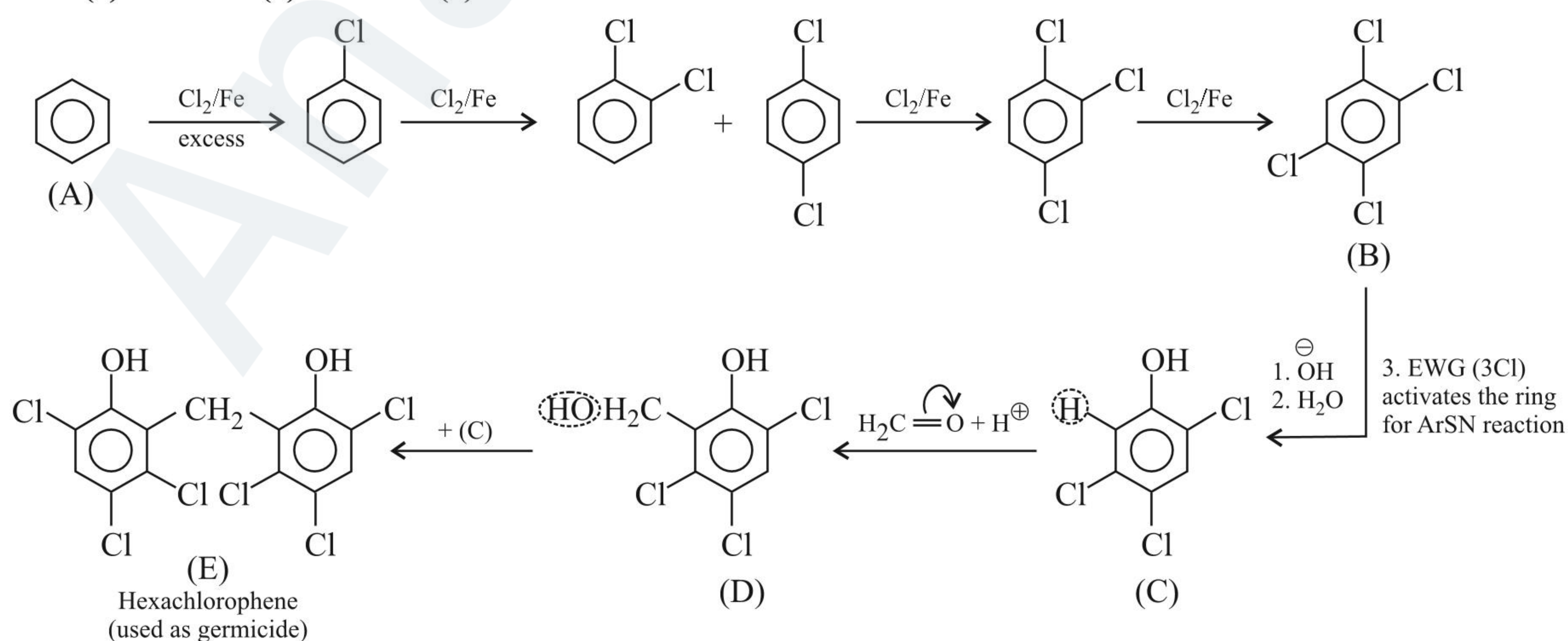
Paragraph 2

6. (3) 7. (1) 8. (1) 9. (1) 10. (2)
 11. (4) 12. (4) 13. (3) 14. (4) 15. (4)



Paragraph 3

16. (3) 17. (3) 18. (1) 19. (1)



Matrix Match Type

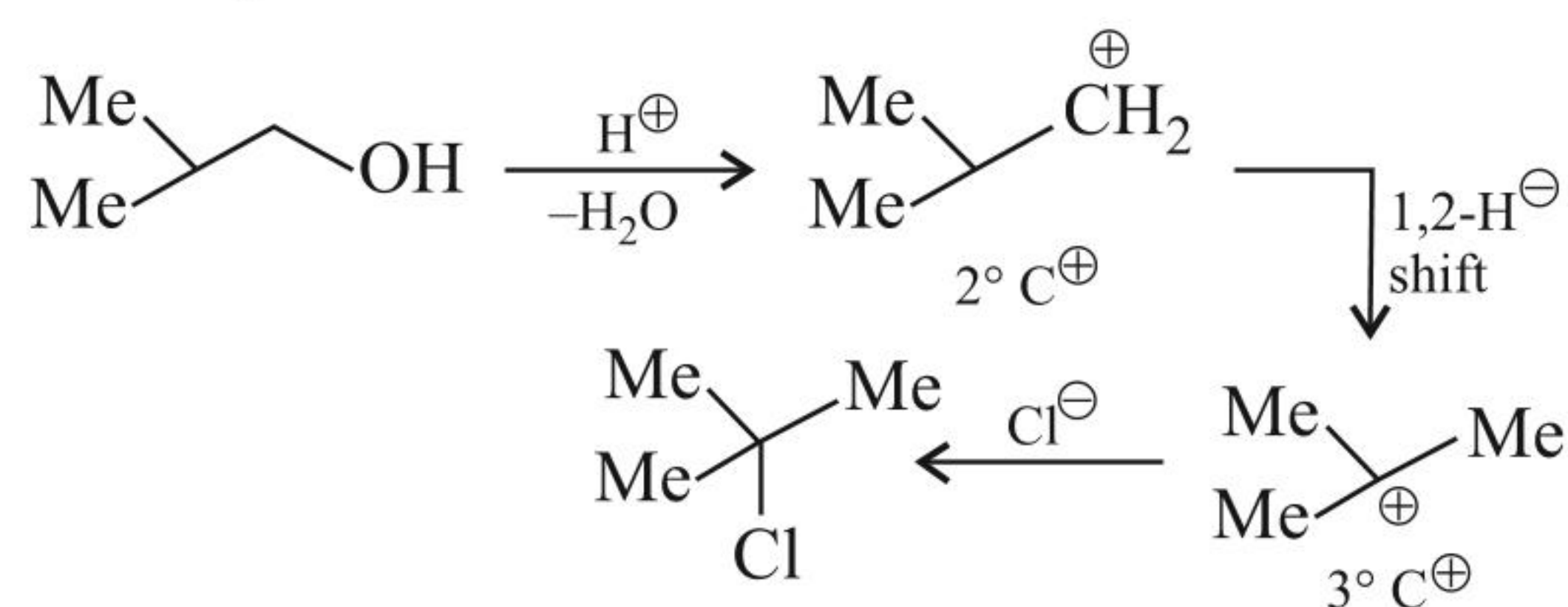
1. (a → q; b → r; c → p, s; d → t; e → u)

The statements are self-explanatory.

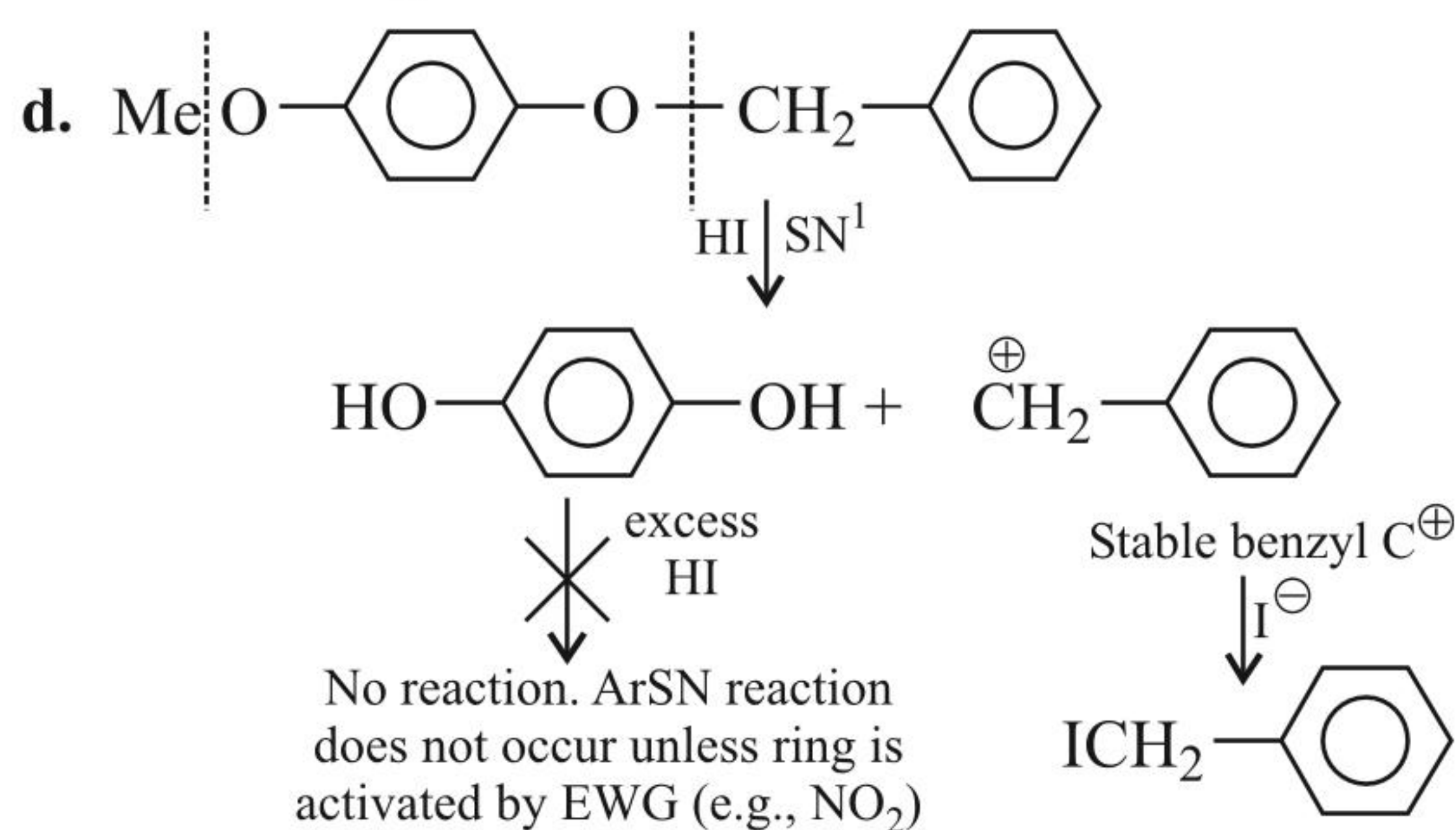
2. (a → q, r; b → p, s, t; c → u; d → p, t; e → p, r, s; f → p, s)

a. Reimer–Tiemann reaction proceeds by (:CBrCl) (bromochlorocarbene), which acts as an electrophile. So, it is an SE reaction.

b. The reaction proceeds by the formation of carbocation with rearrangement.



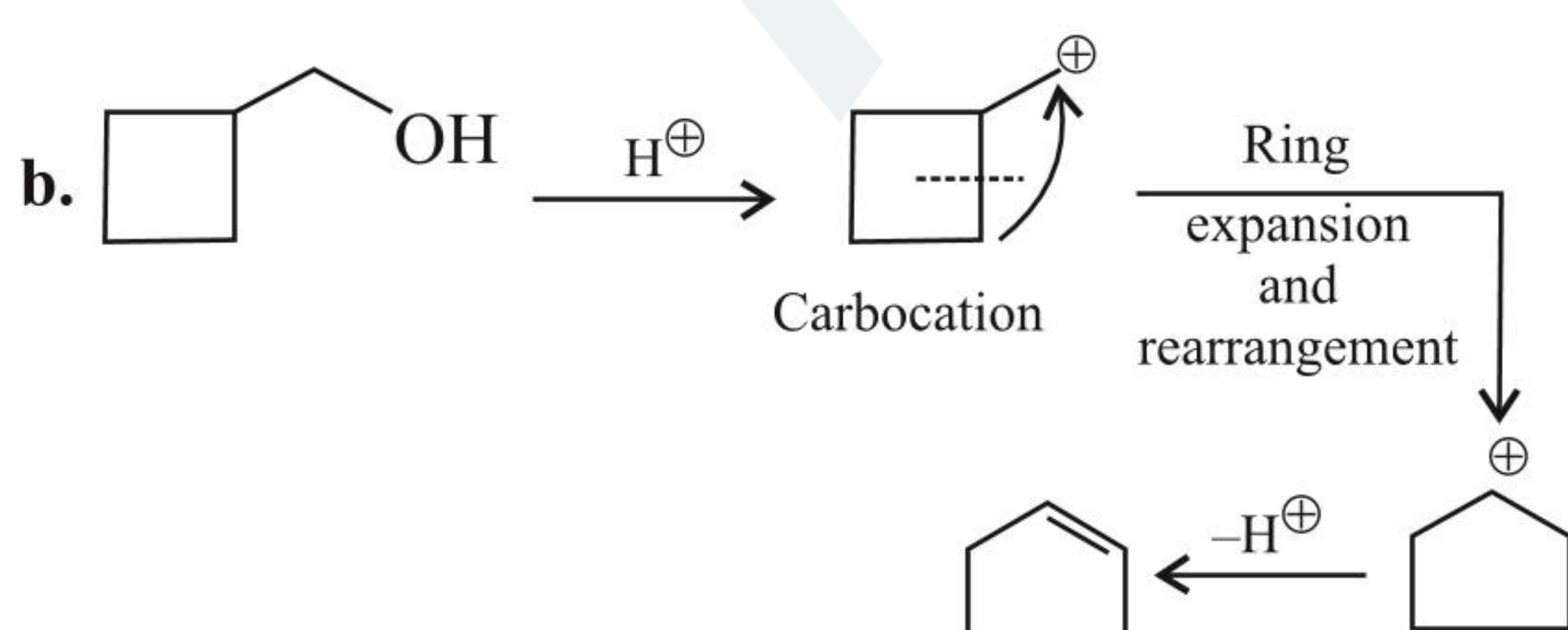
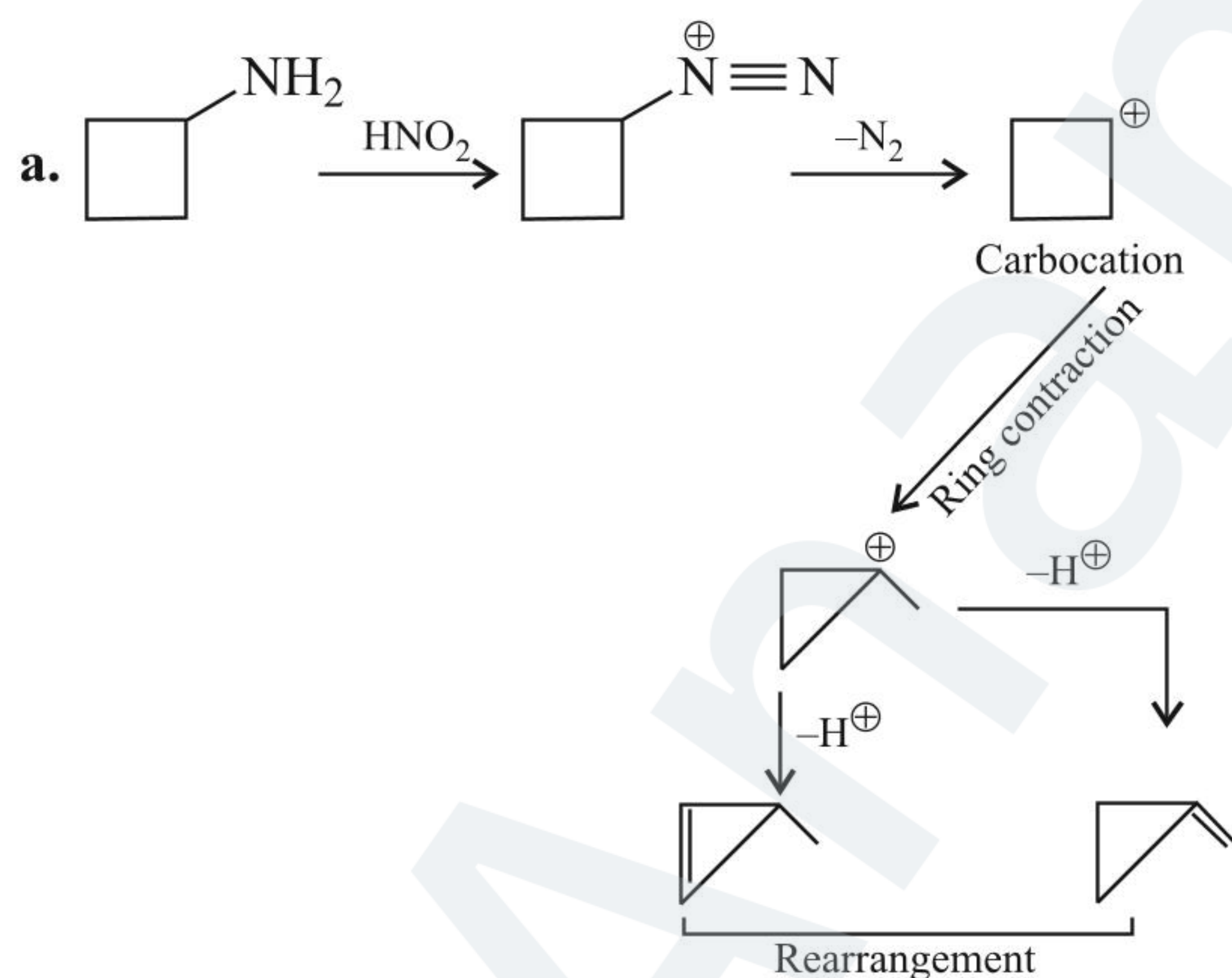
c. No rearrangement occurs since no carbocation is formed.



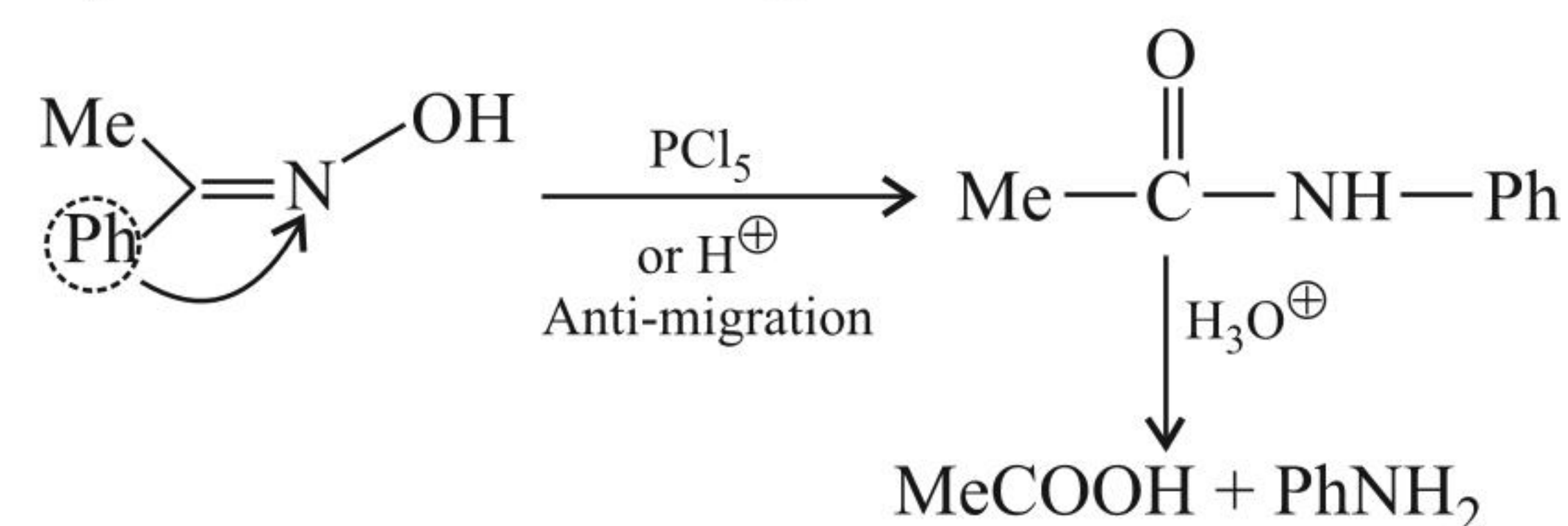
e. It is Friedel–Crafts alkylation which proceeds by the formation of a carbocation followed by rearrangement. So, it is an SE reaction.

f. It is hydration of alkene and proceeds by the formation of a carbocation with rearrangement.

3. (a → q, r, s; b → p, r, s; c → s; d → r, s, t)



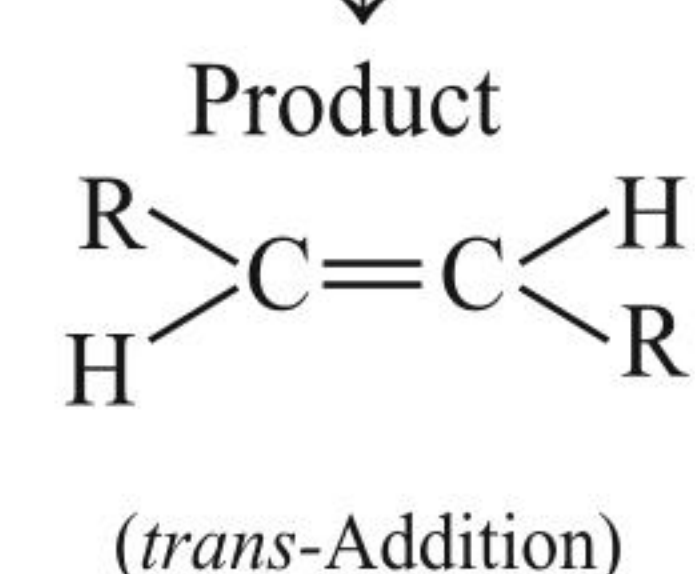
c. It is an example of Beckmann rearrangement reaction.



d. It is an example of bimolecular reduction (formation of pinacol) followed by acid-catalysed rearrangement reaction to form pinacolone. The formation of pinacol proceeds by the formation of a radical anion intermediate.

4. (a → q; b → p, q, r; c → s; d → s)

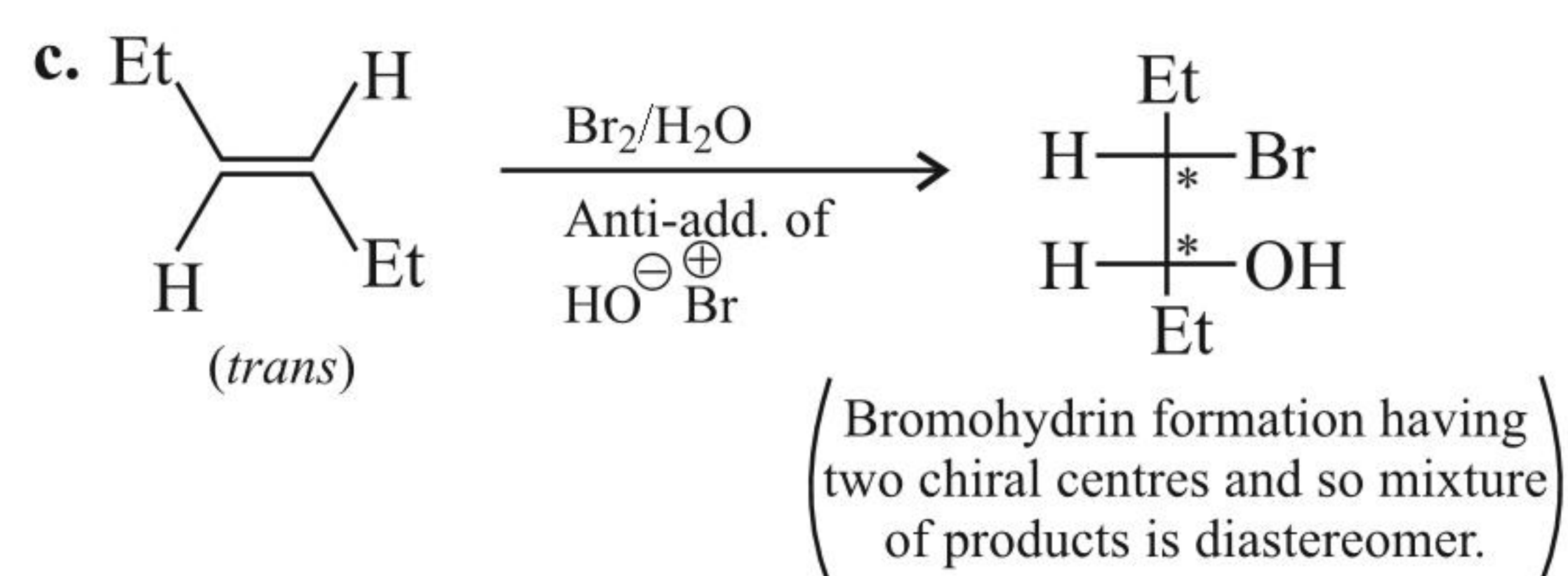
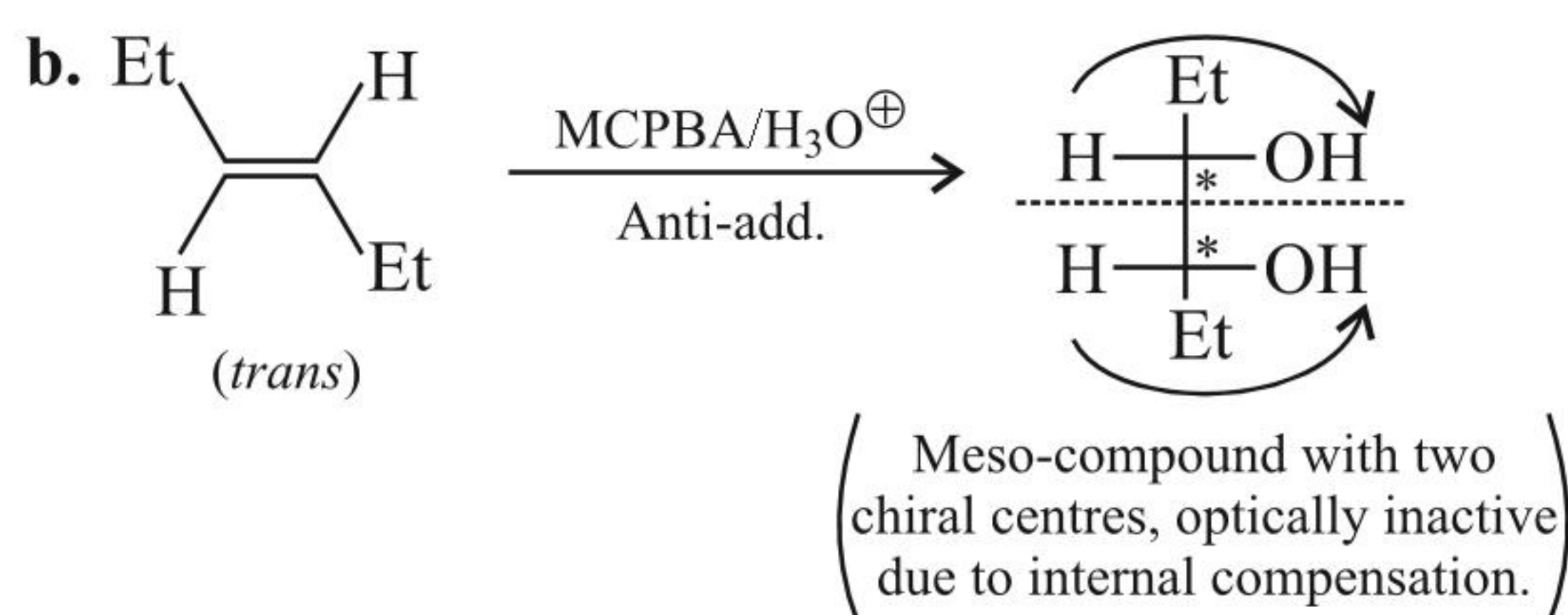
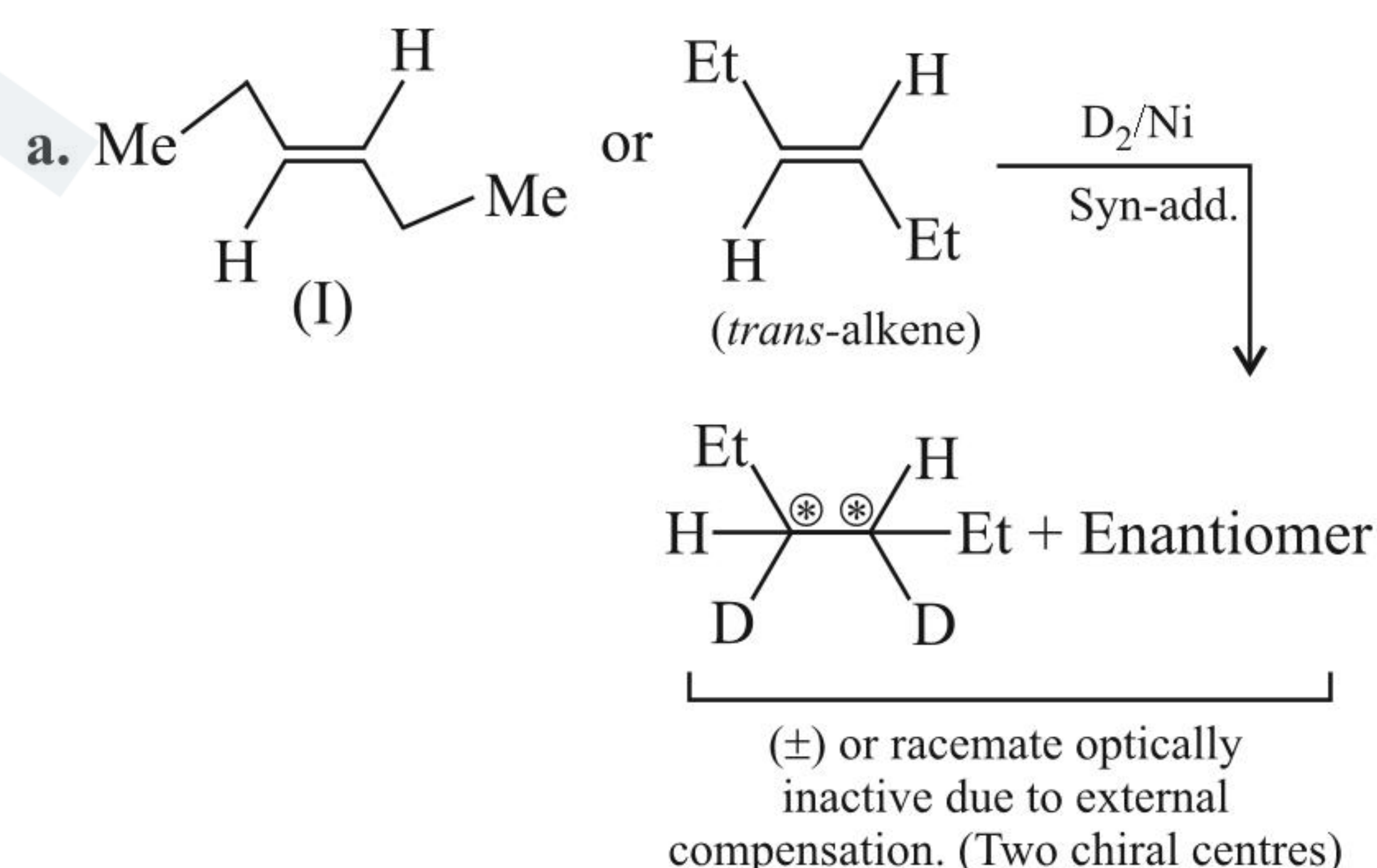
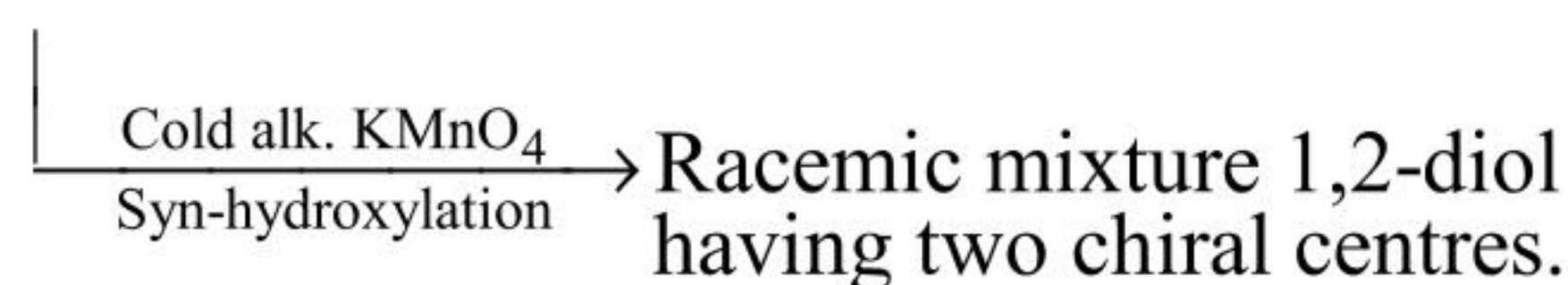
a. It is pinacol formation which proceeds by radical anion.

b. It is Birch reduction which proceeds by the formation of radical anion → vinylic radical → *trans* vinylic anion

c. It is an example of Claisen rearrangement reaction and proceeds by concerted mechanism.

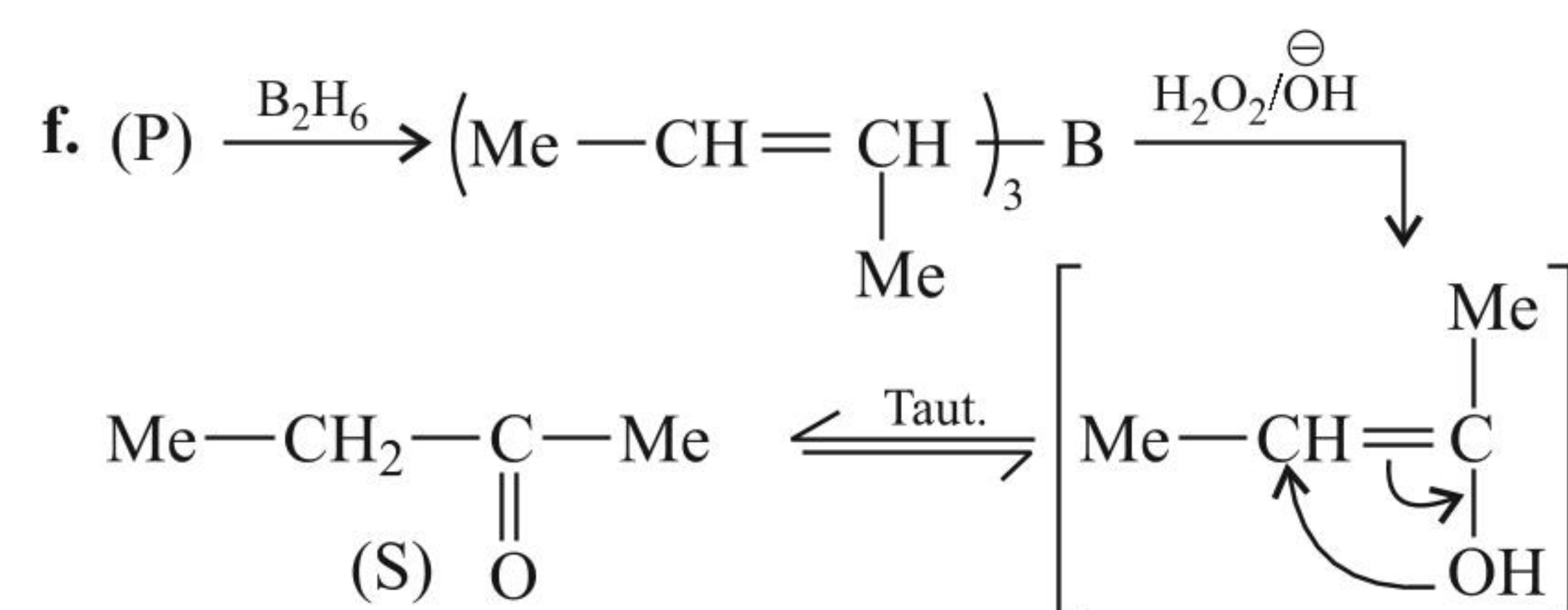
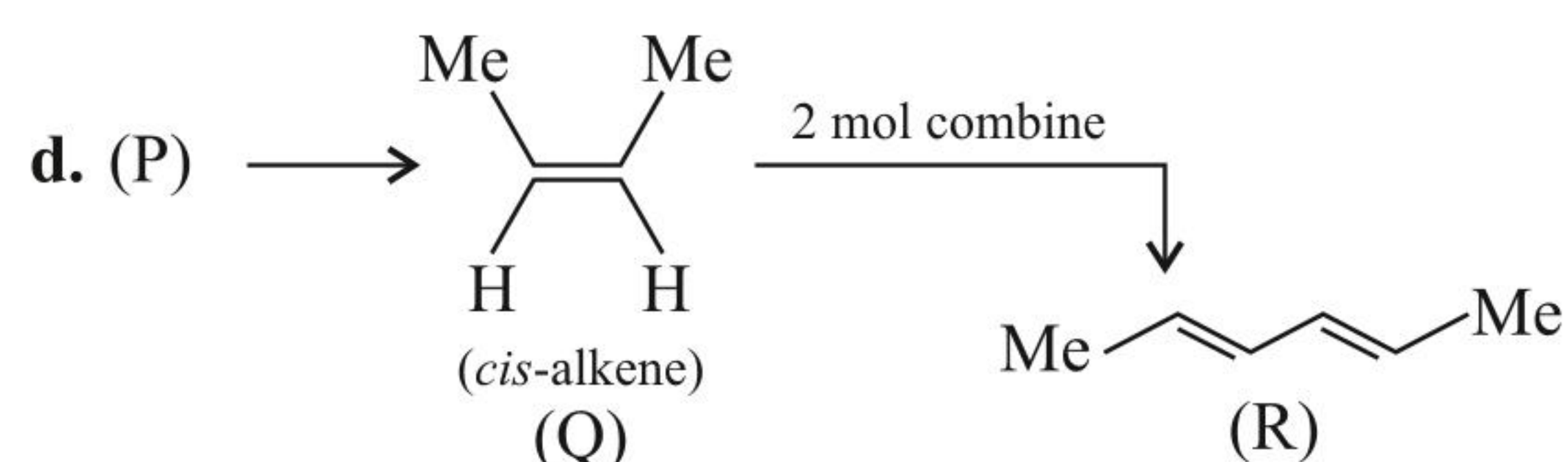
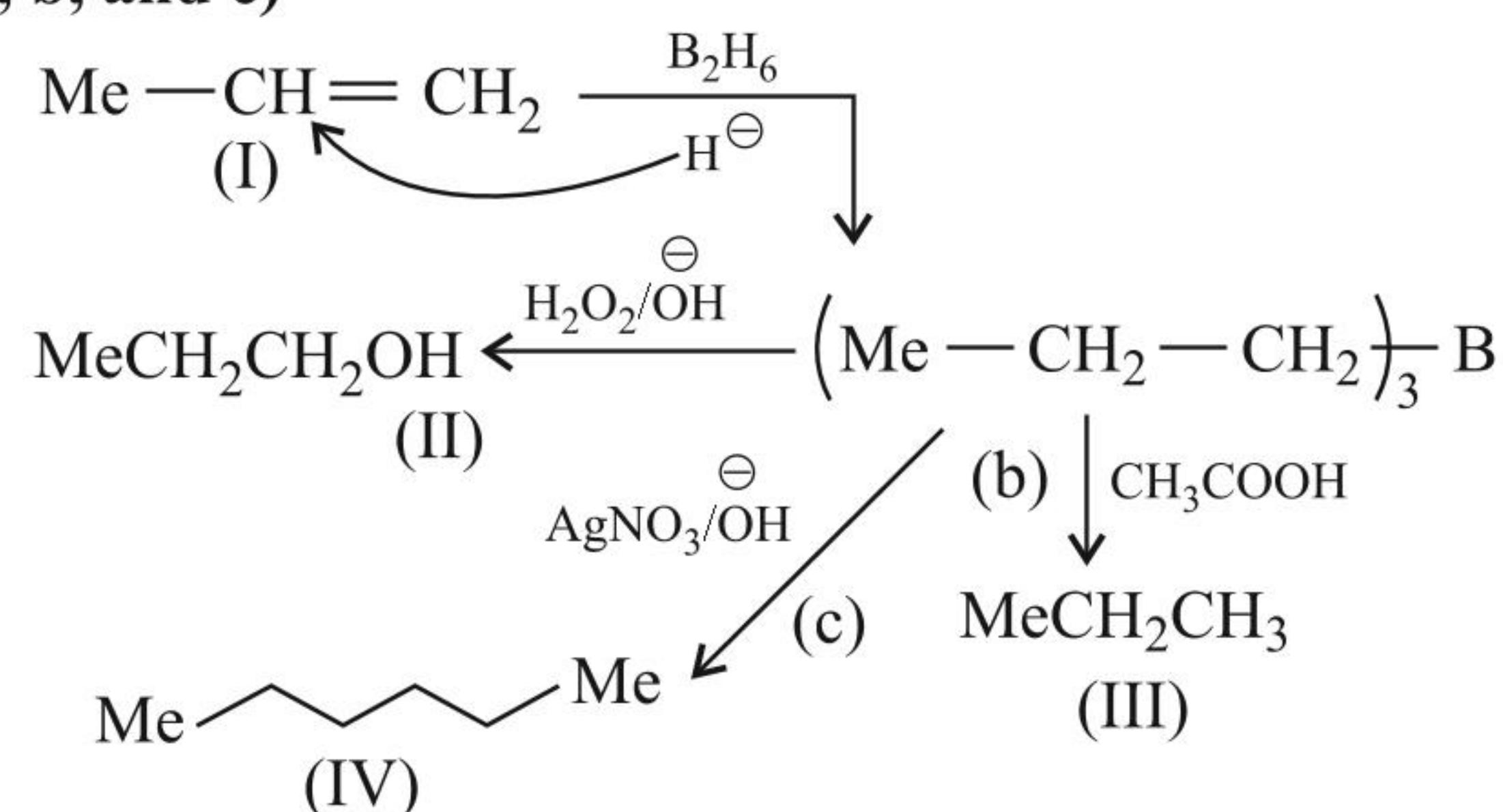
d. It is an example of Diels–Alder reaction and proceeds by concerted mechanism.

5. (a → p, r, s; b → q, s; c → t; d → p, r, s)

d. *trans*-Alkene (I)

6. (a → u; b → p; c → q; d → t; e → s; f → r)

(a, b, and c)



7. (a → ii, p, q; b → i, r; c → iii, p, q, s; d → iv, r)

Refer to illustration 4.13 page 4.26 Organic Chemistry Part - 2

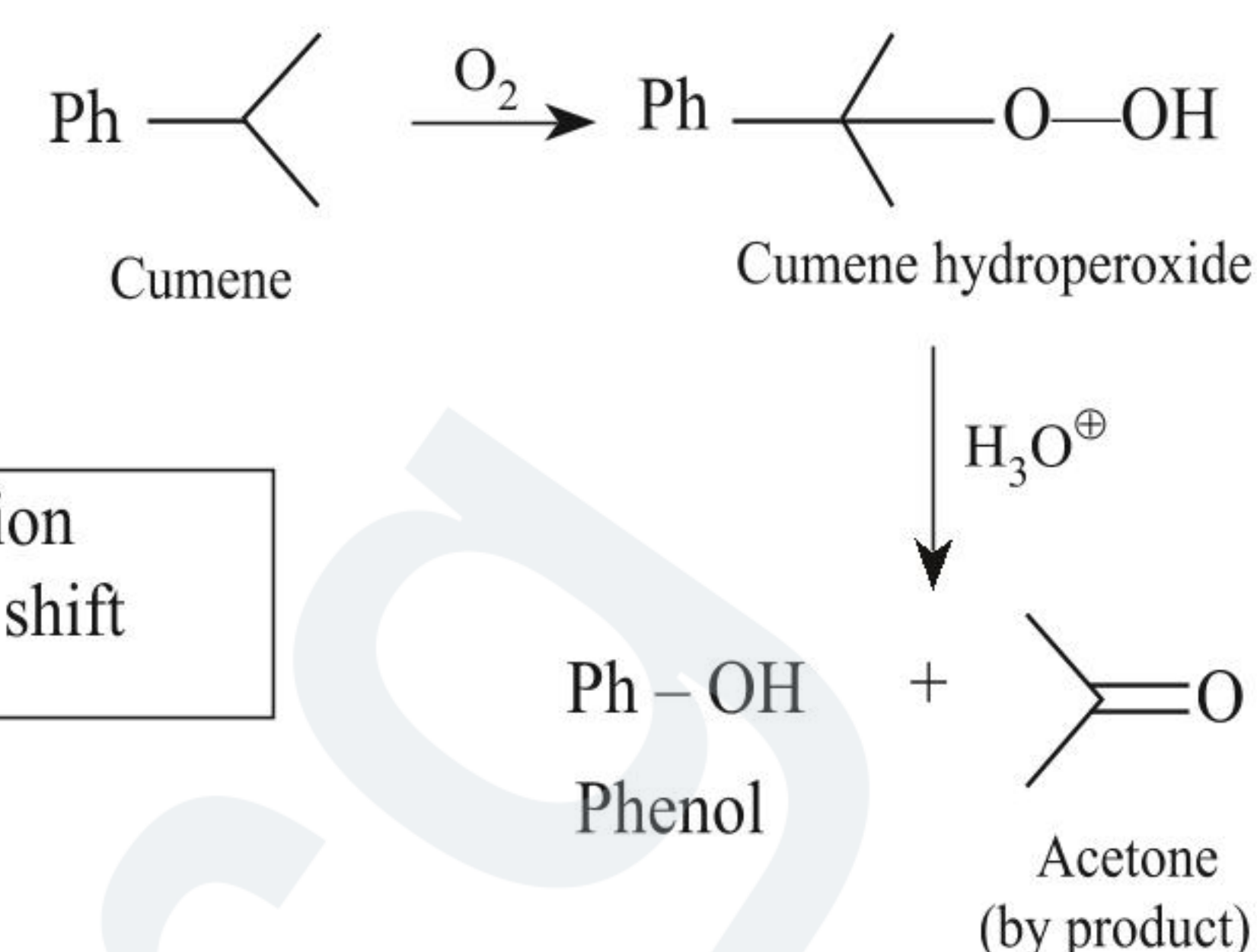
8. (2)

9. (1)

10. (3)

11. (4)

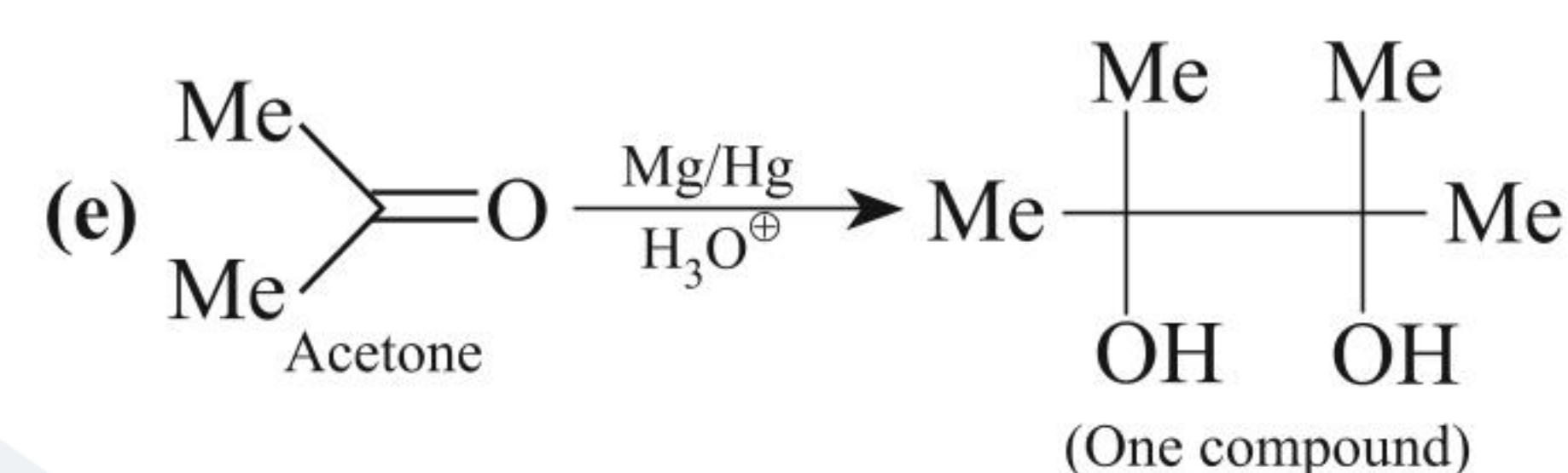
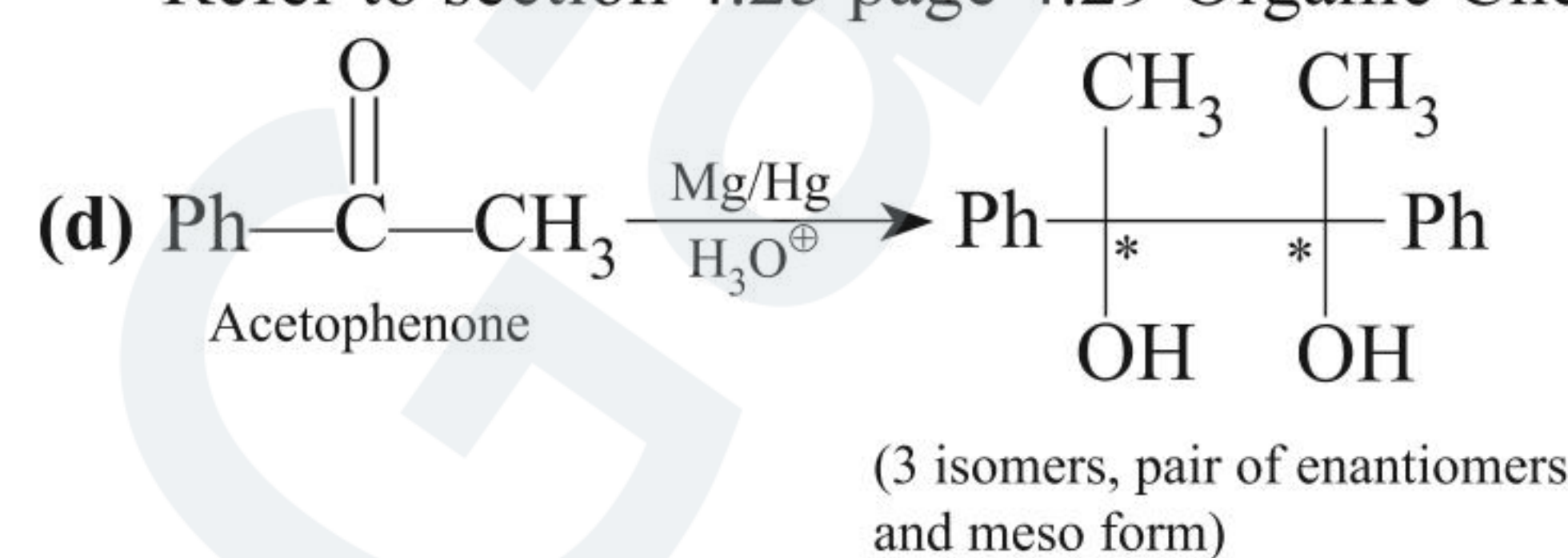
8. (2) a → iv, q

Mechanism of reaction proceed via 1, 2-H⁺ shift

For Q2. (b → iii, p) and for Q3. (c → ii, r) Refer to section 4.15 (iii) page 4.71 Organic Chemistry Part - 2

11. (4) (d → i, s)

Refer to section 4.25 page 4.29 Organic Chemistry Part - 2



Numerical Value Type

1. (8) i. Write the five C atoms straight chain and put (—OH) group at different positions.

	(I)	[(II) + (III)] (O.A)	(IV)
IUPAC	Pentan-1-ol	(±)-Pentan-2-ol	Pentan-3-ol
Common	n-Amyl alcohol	—	—
Carbinol	n-Butyl carbinol	Methyl propyl carbinol	Diethyl carbinol
Type	1°	2°	2°

ii. Write the four atoms in straight chain and put Me and (—OH) at different positions.

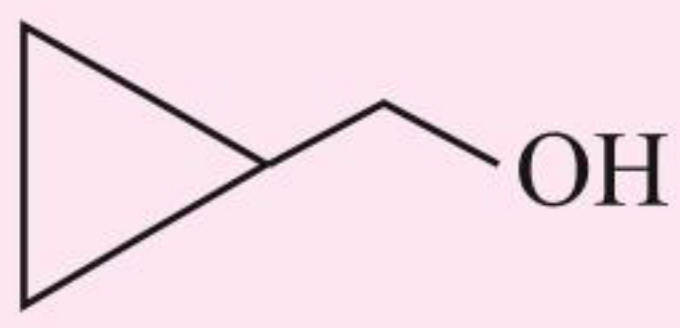
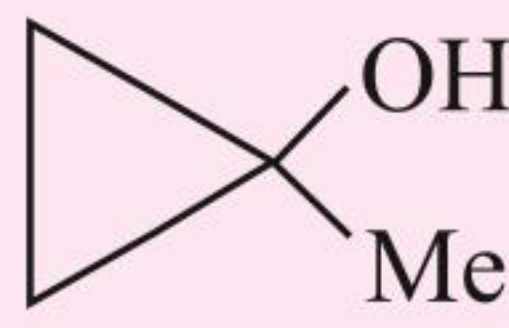
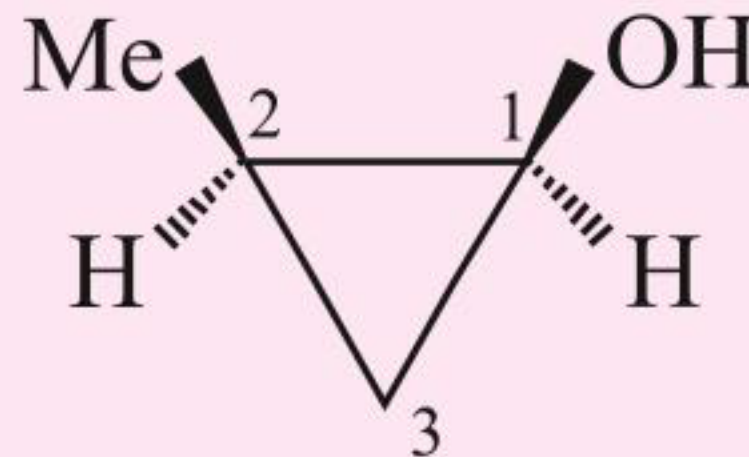
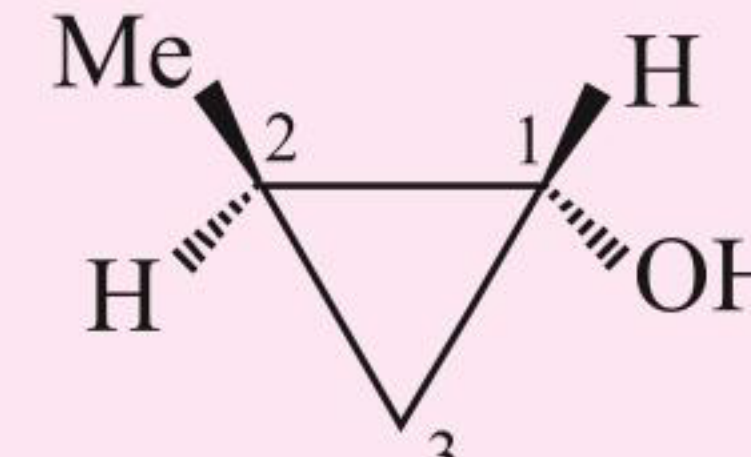
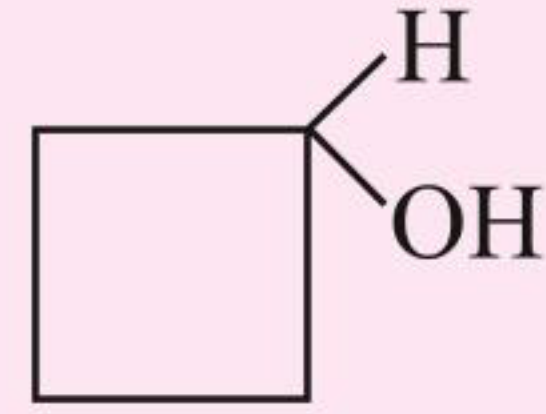
	[(V) + VI] (O.A)	(VII)
IUPAC	(±)-3-Methyl butan-2-ol	2-Methyl butan-2-ol
Common	—	t-Pentyl alcohol
Carbinol	Isopropyl methyl carbinol	Dimethyl ethyl carbinol
Type	2°	3°

iii. Write the three C atoms in straight chain and but two Me and (—OH) at different positions.

	(VIII)
IUPAC	2,2-Dimethyl propan-1-ol
Common	Neopentyl alcohol
Carbinol	t-Butyl carbinol
Type	1°

Hence, total isomers including stereoisomers of C₅H₁₂O are 8.

2. (7)

 (I)	 (II)	 (III + IV) O.A.	 (V + VI) O.A.	 (VII)
Cyclopropylmethanol	1-Methylcyclopropanol	(±) or <i>r-cis</i> -2-Methylcyclopropan-1-ol	(±) or <i>r-trans</i> -2-Methylcyclopropan-1-ol	Cyclobutanol

Hence, total isomers including stereoisomers of C_4H_7OH are 7.

3. (3) 2.68 gm of (A) gives 14.08 gm of AgI

$$134 \text{ gm of (A) gives } \frac{14.08 \times 134}{2.68} = 704 \text{ gm of AgI}$$

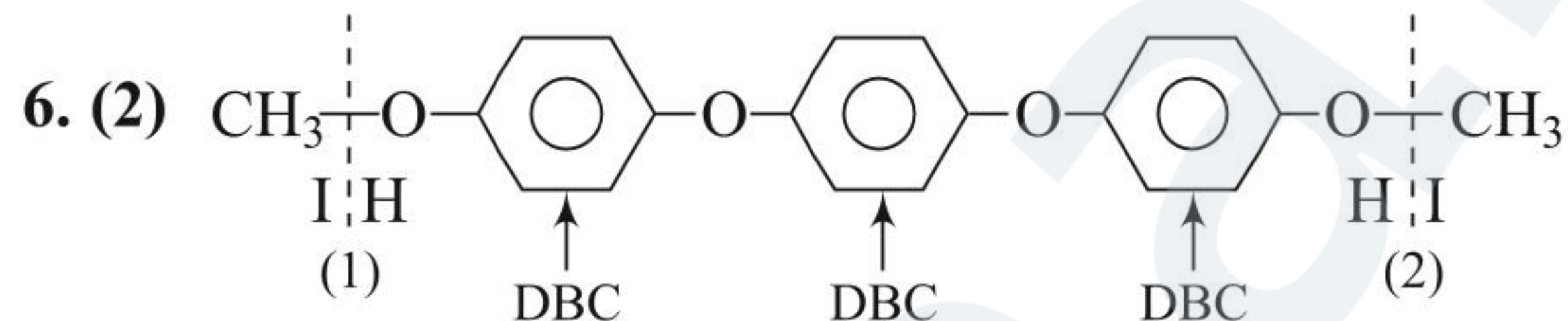
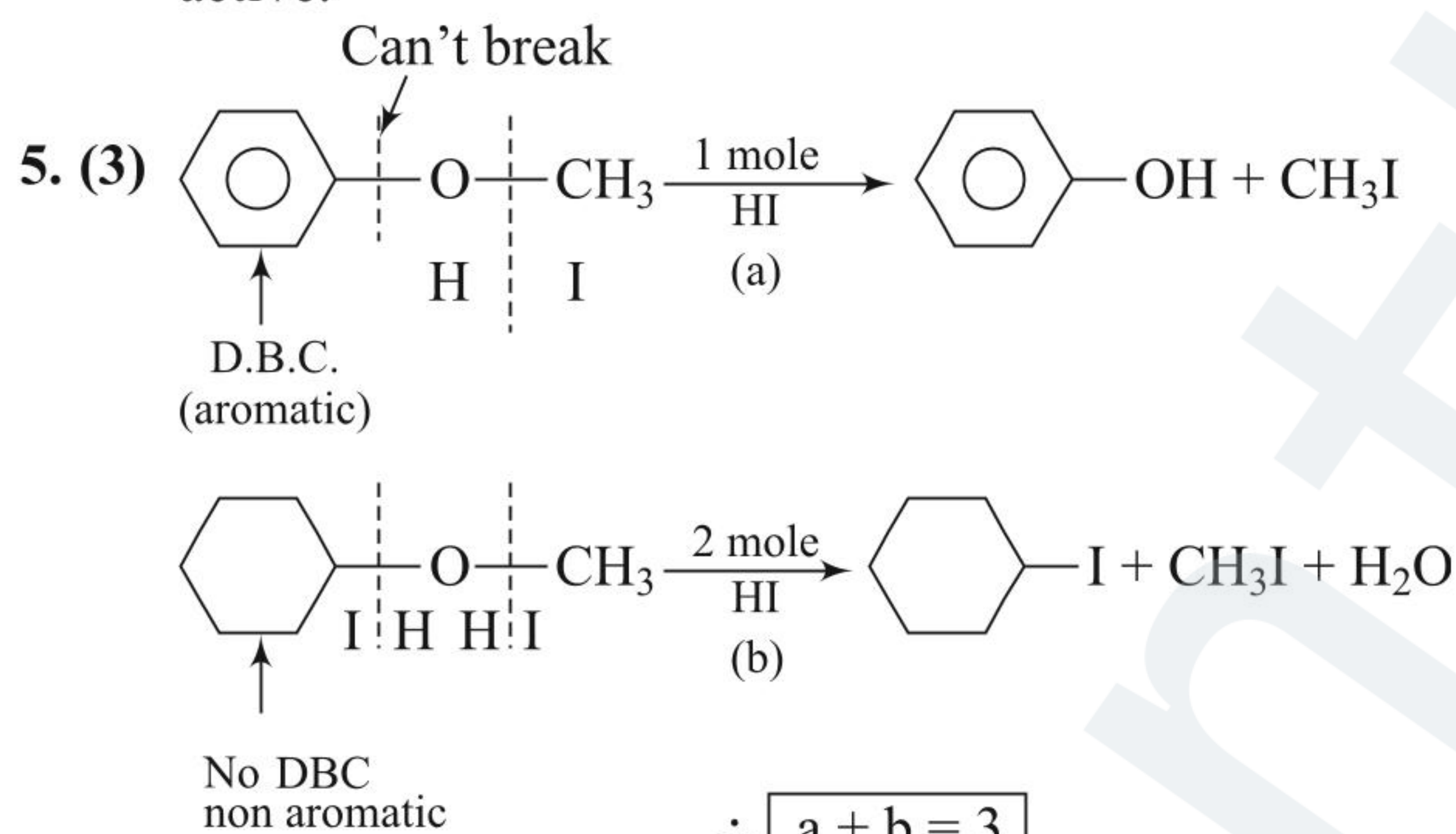
$$= \frac{704}{235} = \text{mol of AgI} = 3 \text{ (OMe) groups}$$

4. (4) (dl) 2-methyl butanoic acid and (dl) 2-butanol

⇓ esterification

(d, d) Ester (1) (l, l) Ester (2) (d, l) Ester (3) (l, d) Ester (4)

Ester consists of two stereocentres. Chiral center during whole reaction are not effected, that's why all esters are optical active.

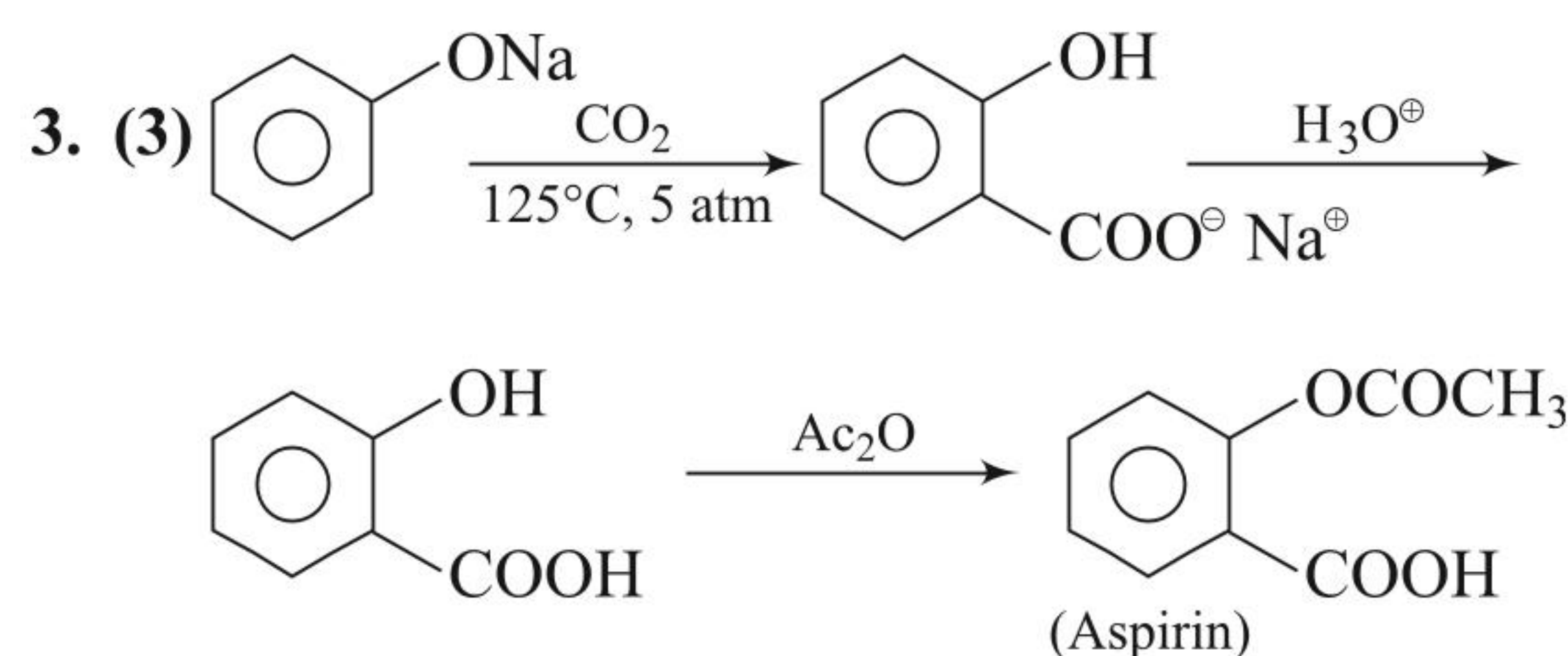
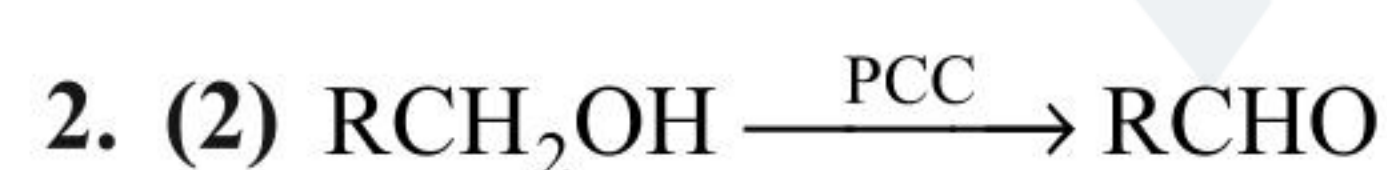
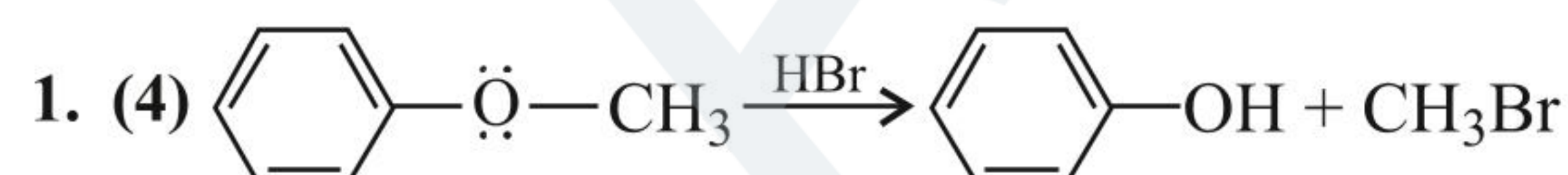


7. (6) and 8. (6) [Refer to Illustration 4.2.]

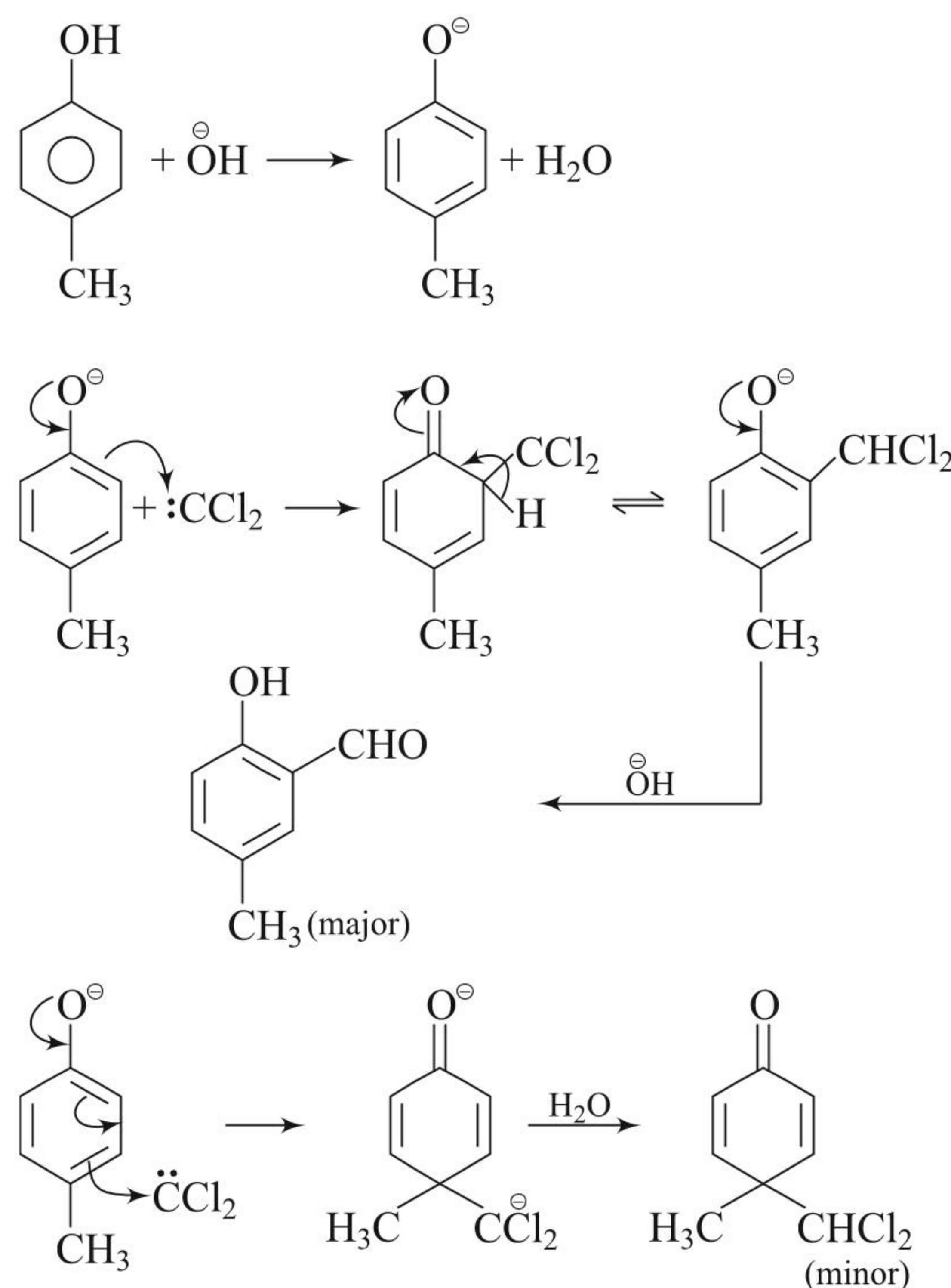
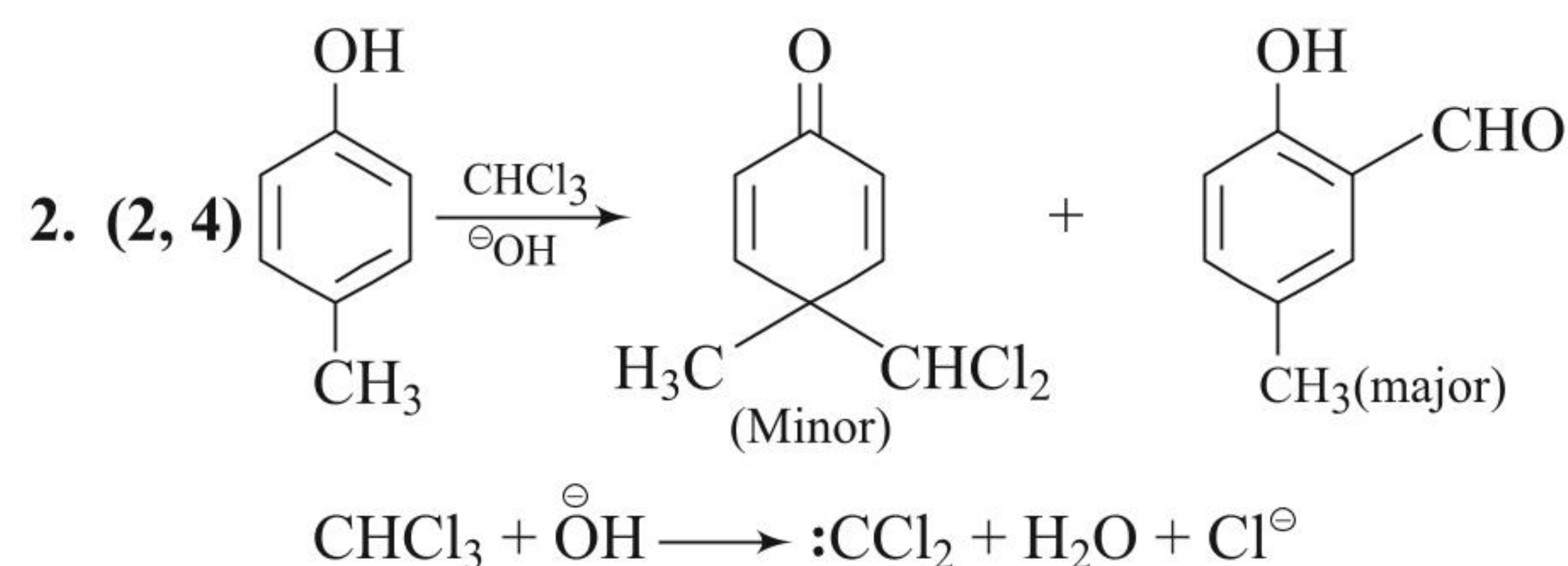
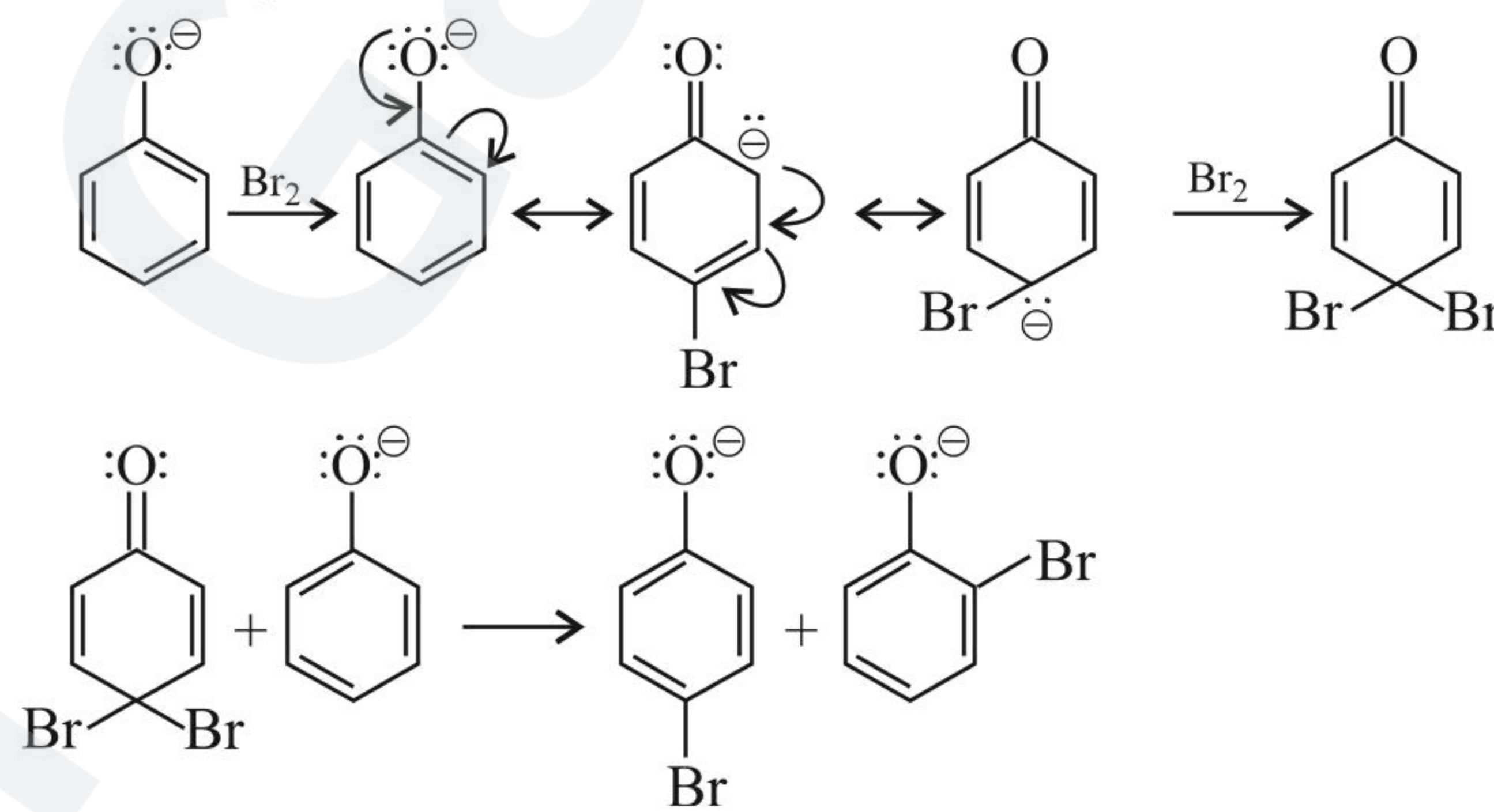
Archives

JEE Advanced

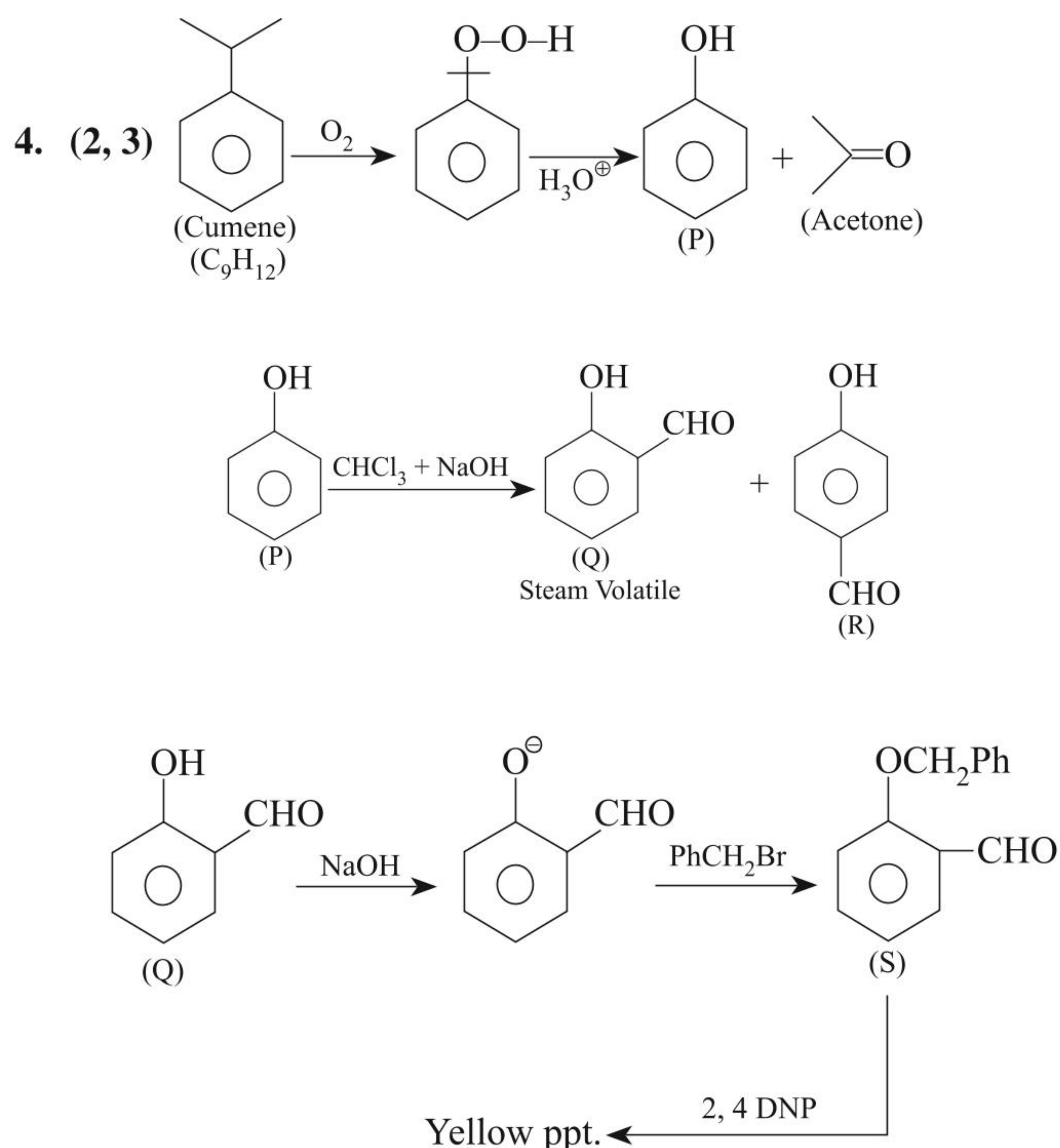
Single Correct Answer Type

4. (3) *p*-Methoxy phenyl group is EDG, which can stabilise carbocation.

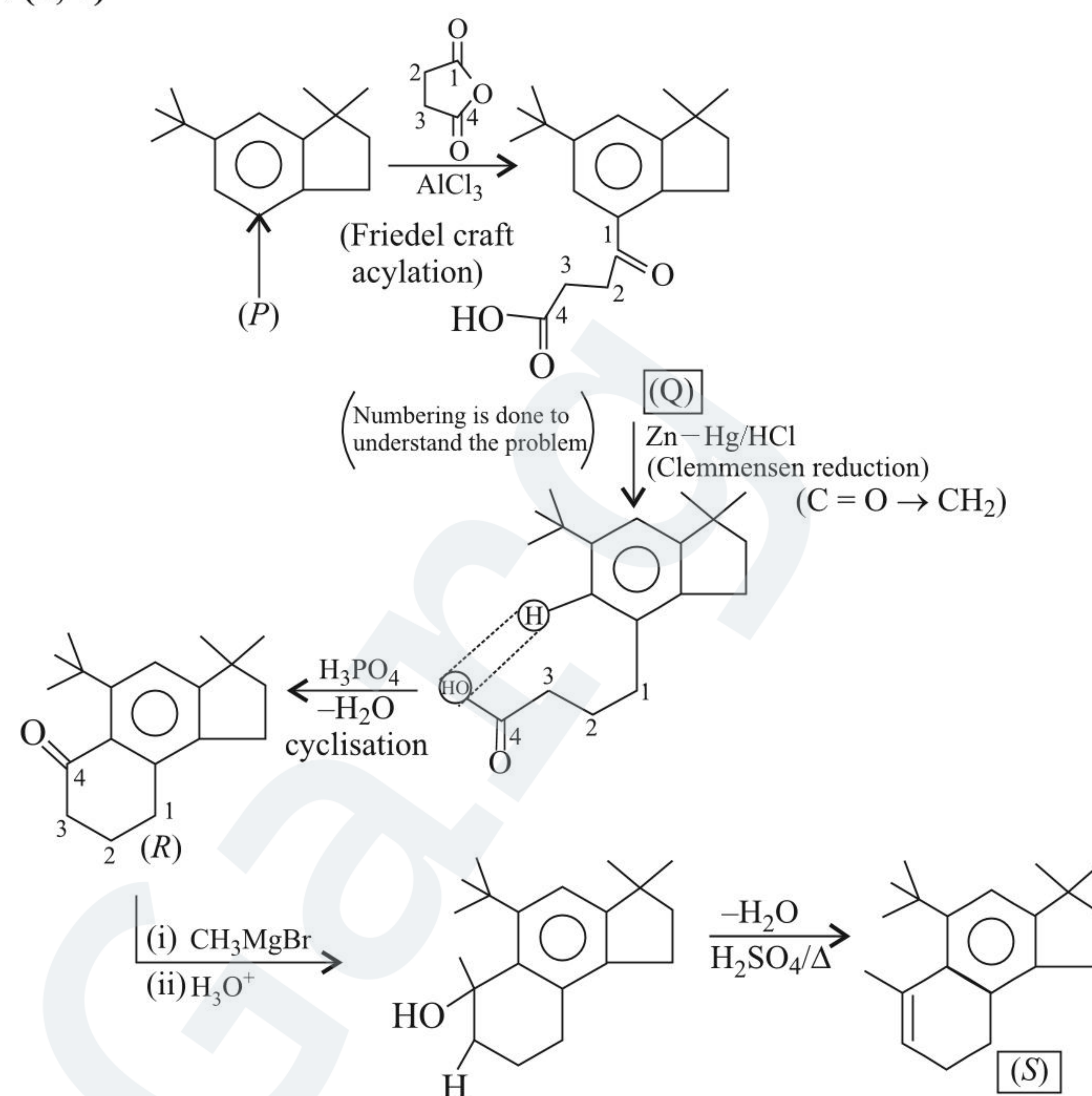
Multiple Correct Answers Type

1. (1, 2, 3) Phenoxide ion is *para* and *ortho* directing, preferably *para*.

3. (1, 3, 4) factual statement

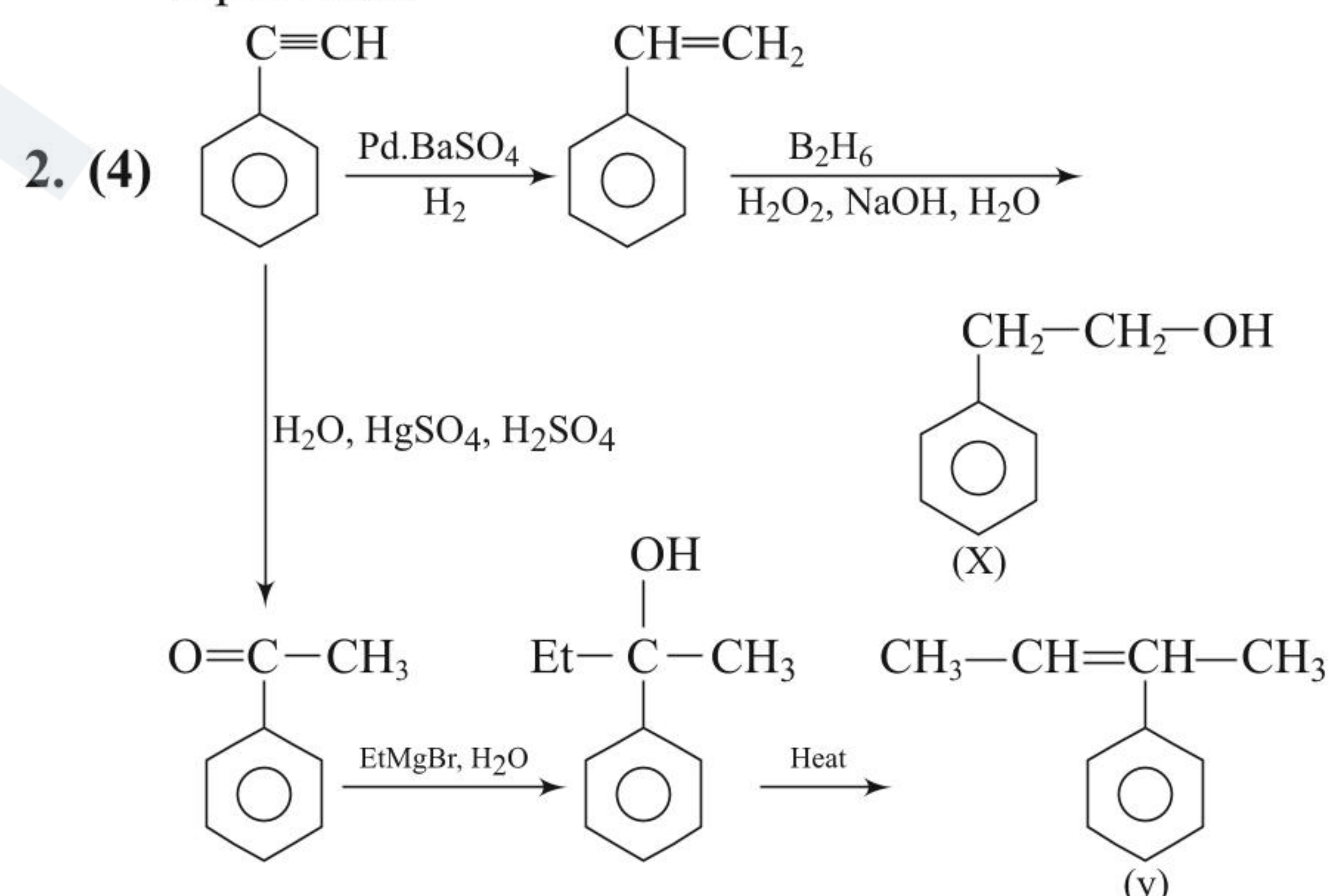


7. (2, 4)



Linked Comprehension Type

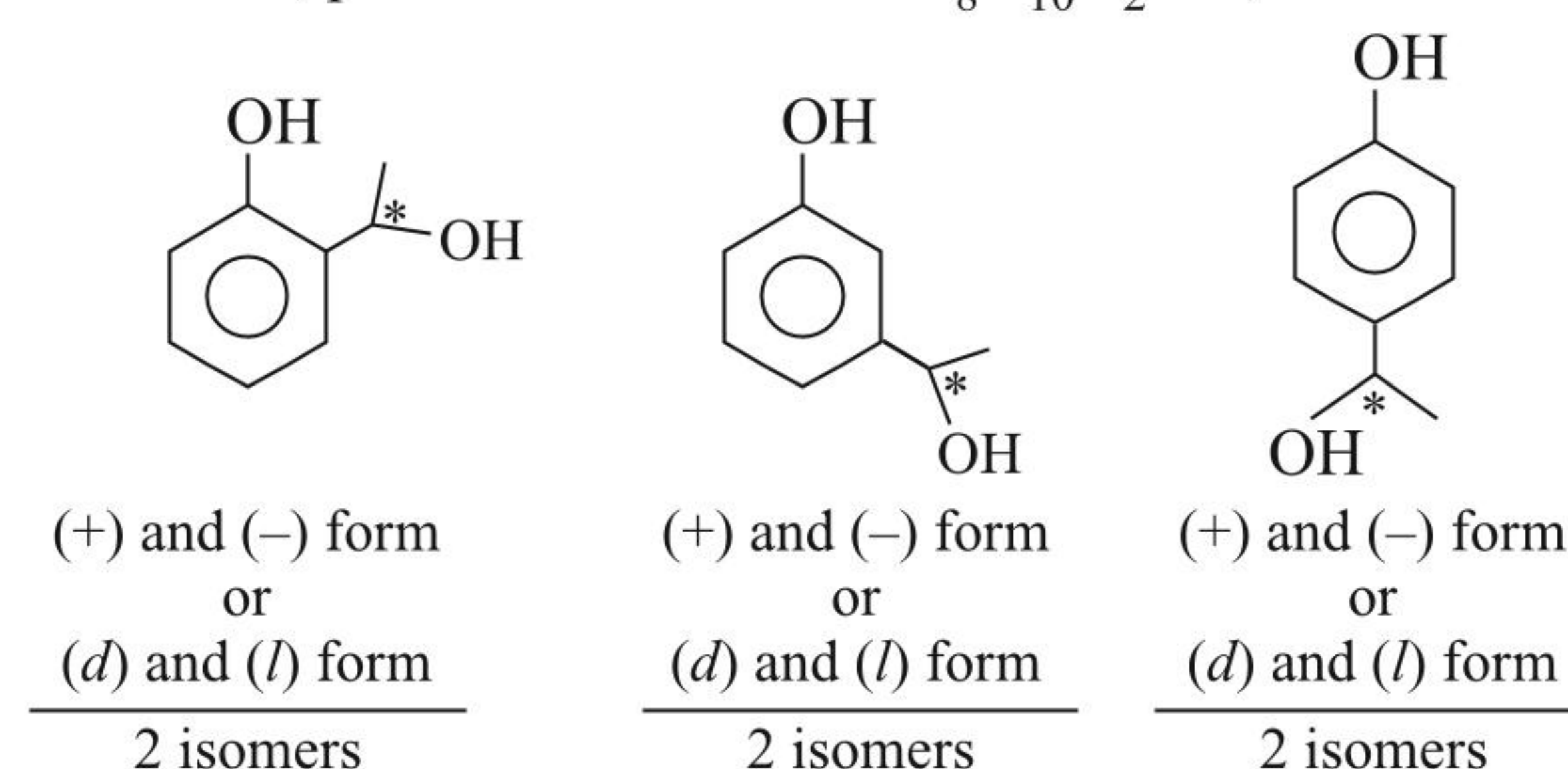
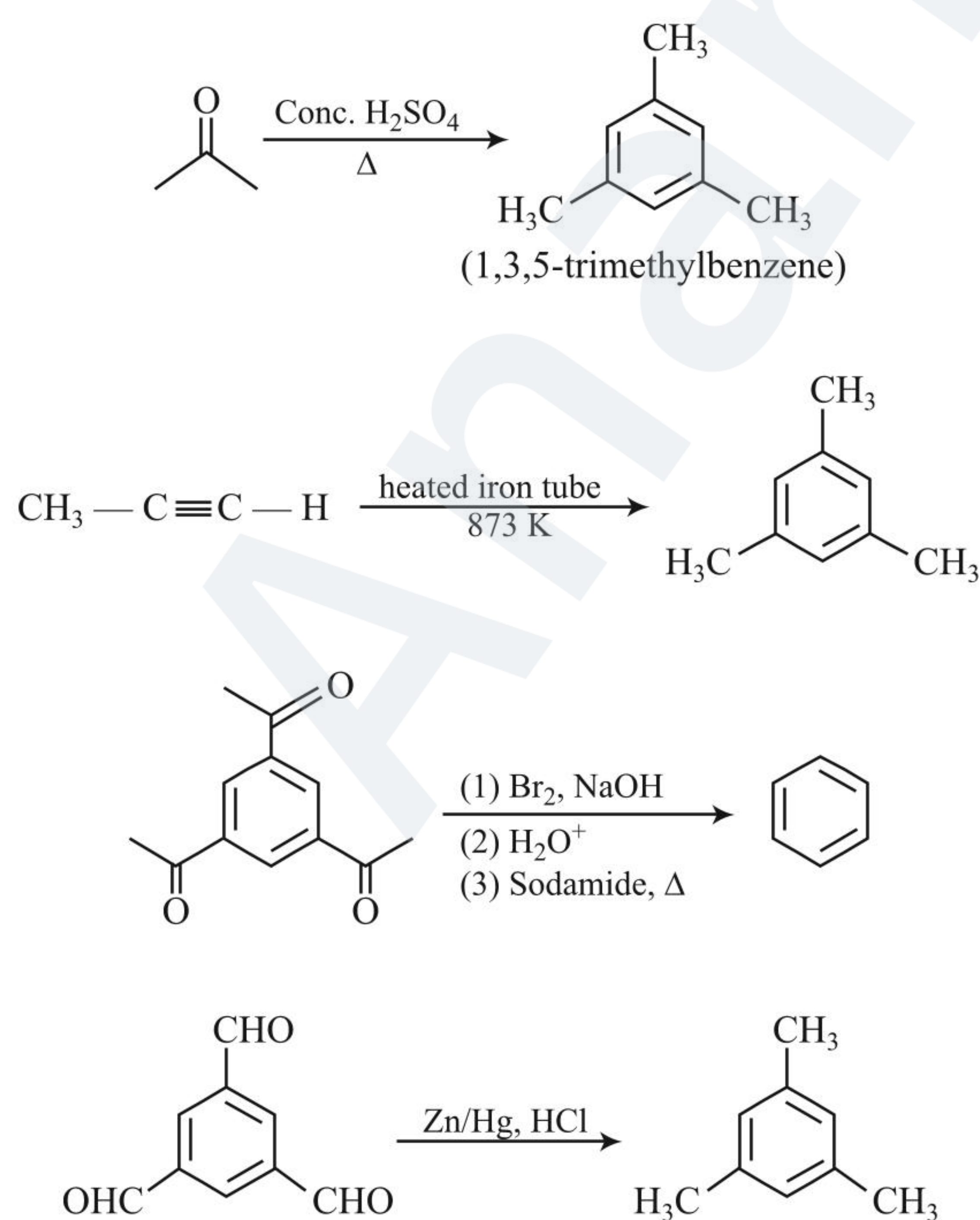
1. (3) DU in $C_8H_6 \Rightarrow C_8H_{18} \Rightarrow \frac{18-6}{2} = 6^\circ$, 4° for benzene & 2° for triple bond.



Numerical Value Type

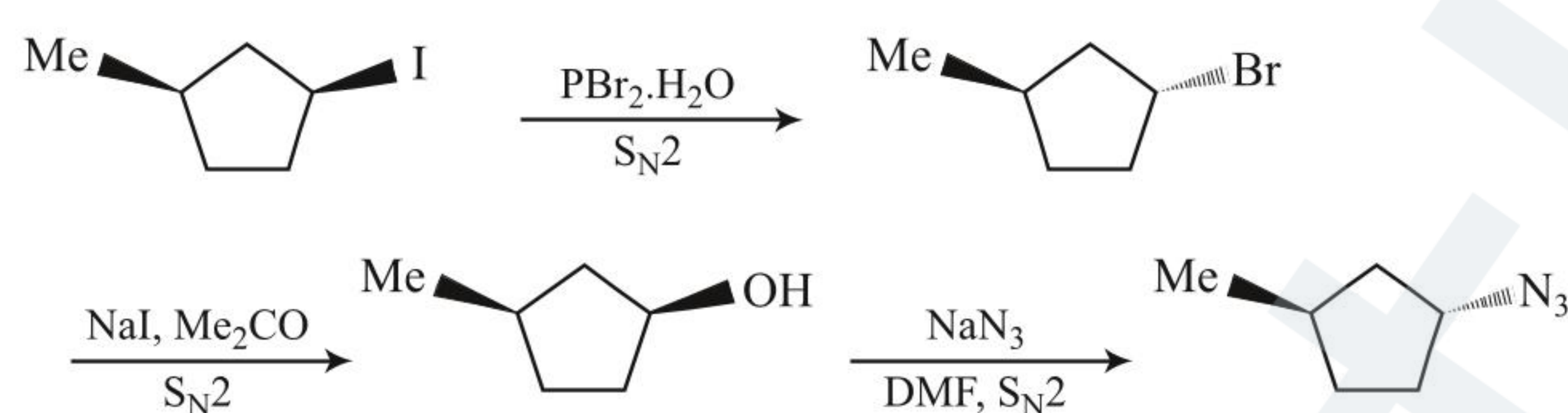
1. (6)

- DU of the given compound $C_8H_{10}O_2$ is 4° suggests that it contains benzene ring.
- The given compound gives pink colour with neutral $FeCl_3 \Rightarrow$ It is phenolic compound.
- The given compound is optically active, suggests that it contains chiral centre, i.e., it has $-CH(OH)CH_3$ group.

Therefore, possible structures of $C_8H_{10}O_2$ are,

So, total isomers = 6.

5. (2)



6. (1, 2, 4)